Characterization of nitrous acid and its potential effects on secondary pollution in warm-season of Beijing urban areas

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Abstract. As a key source of hydroxyl (OH) radical, nitrous acid (HONO) has attracted much attention for its important role in the atmospheric oxidant capacity (AOC) increase. In this study, we made a comparative study on the ambient levels, variation patterns, sources, and formation pathway in warm season (from June to October in 2021) on a basis of a continuous intensive observation in an urban site of Beijing. The monthly average mixing ratio of HONO were 1.3 ppb, 1.3 ppb, 1.0 ppb, 0.96 ppb, 0.89 ppb, respectively, showing a larger contribution to OH radical relative to ozone at daytime. The emission factor (EF) relative to NO_x from the vehicle emissions, was estimated to be 0.017, higher than most studies conducted in Beijing. The average nocturnal NO_2 to HONO conversion frequency k_{HONO} were 0.008 h^{-1}. In warm seasons, the missing source of HONO, $P_{unknown}$, around noontime were 0.29-2.7 ppb/h. According to the OH production from HONO, the OH production rate from the missing HONO was also very important to atmospheric oxidation capacity (AOC). This work highlights the importance of HONO for AOC in warm season, while encouraging long-term HONO observation to assess the contribution of HONO sources over time compared to the capture of pollution processes.

1 Introduction

From 2013 to 2022, the annual average concentration of $PM_{2.5}$ in China has been decreasing, but it is still much higher than the World Health Organization's guideline value (5 μg/m^3). Ozone pollution, on the other hand, is becoming more and more prominent (Liu et al., 2023b;Li et al., 2022). China's air quality problem has developed from being dominated by $PM_{2.5}$ in the past to being affected by the photochemical pollutants $PM_{2.5}$ and ozone, that is, “Air Pollution Complex” (Zhu et al., 2023). The atmospheric oxidation capacity (AOC) determines the production rates of secondary pollutants in the atmosphere, and is the essential driving force in forming complex air pollution (Liu et al., 2021b).

As a trace gaseous pollutant, nitrous acid (HONO) strongly impacts the AOC, the photolysis of which can contribute to more than 60% of the OH radicals at daytime (Czader et al., 2012). As an important source of OH radicals in both rural and urban environments, HONO outweighs the contribution of ozone photolysis (Gu et al., 2022;Elshorbany et al., 2012;Yang et

al., 2021b). Thus, as an important source of oxidants for AOC, HONO can substantially influence the formation of secondary pollutants, exerting a considerable impact on air quality, climate change, and human health (Requia et al., 2018;Zhang et al., 2021b;Huang et al., 2018;Liu et al., 2023b).

Due to the importance of HONO to AOC, researchers have done lots of work on the transformation process of HONO, i.e., source and sink. For the source of HONO, it is complicated and has been debated for decades. To sum it up, source of atmospheric HONO mainly includes: (a) direct emission from combustion, soil, and livestock farming. The combustion includes vehicle exhaust, industrial exhaust, and biomass burning (Liao et al., 2021;Kurtenbach et al., 2001;Kirchstetter et al., 1996;Nie et al., 2015). The release from soil nitrite is one important primary source of HONO (Su et al., 2011; VandenBoer et al., 2015; Wu et al., 2019), the biological soil crusts can accelerate the HONO emission in drylands (Weber et al., 2015), fertilization behavior of agricultural fields remarkably enhance the emission of HONO (Xue et al., 2021), and denitrification is one major HONO production pathway in boreal agricultural fields (Bhattarai et al., 2021). Meanwhile, livestock farming is also identified as one important primary emission source of HONO (Zhang et al., 2023a). (b) Homogeneous reaction of OH +NO. This is an important source of HONO. Although the reaction of OH+NO, which is the reverse reaction of HONO photolysis, does not contribute to an actual increase in free radicals, the assessment of this reaction pathway is significant for understanding the sources and sinks of HONO. Especially during the winter pollution period in North China Plain, where there is usually a higher concentration of NO, this reaction pathway will contribute to a higher concentration of HONO (Xue et al., 2020). (c) Heterogeneous conversion of NO_2 on various surfaces (Liu et al., 2023a;Yu et al., 2022a;Yang et al., 2021a), Finlayson-Pitts et al. (2003) reported that NO_2 could be converted to HONO on humid surfaces with first order in NO_2, Xu et al. (2015) highlighted the HONO source had a large variability with heterogeneous conversion of NO_2 at ground face, Aubin and Abbatt (2007) found that the heterogeneous conversion of NO_2 on hydrocarbon surfaces was an effective pathway to generate HONO. (d) photolysis of nitric acid and nitrate in particles at daytime, which were considered as important sources of HONO in both experiments and field observations (Wang et al., 2023b;Ye et al., 2019;Yang et al., 2018;Ye et al., 2017). And for the sinks of HONO, diurnal photolysis is the main consumption way (Keller-Rudek et al., 2013), the reaction of HONO with OH radical is also one sink that needs to be paid attention to (Cox et al., 1976).

Generally, HONO concentration in the atmosphere is closely related to the quality of the atmosphere. As the heterogeneous processes are considered as the main source of HONO, and most of which are poorly understood, therefore, many field observations of HONO were focus on haze polluted environments (Li et al., 2012;Spataro et al., 2013;Tong et al., 2015;Xu et al., 2015;Hou et al., 2016). In urban areas, the HONO concentration can be up to more than 10 ppb during severe pollution episode (Zhang et al., 2019b). In China, the Chinese government has implemented series of stringent clean air actions to address the severe air pollution issue since 2013, significant reduction of $PM_{2.5}$ was observed in North and South China during 2013-2020 (Li et al., 2022). However, ozone levels have not been effectively reduced in China, the warm-season (from April to September) mean maximum daily 8 h average ozone (MDA8 O_3) increased by 2.6 μg/(m^3·yr) (Liu et al., 2023b). In view of the atmospheric changes in $PM_{2.5}$ and ozone, recent field observations have begun to pay attention to the potential influence of HONO on $PM_{2.5}$, ozone, and coexistence of $PM_{2.5}$ and ozone (Zhang et al., 2023c;Zhang et al.,

2023b;Xuan et al., 2023;Chen et al., 2023;Zhang et al., 2022;Lin et al., 2022;Li et al., 2021). However, most HONO observations were conducted in autumn and winter, and the period were relatively short, usually a few weeks covering one or several pollution processes. Based on the increase of ozone in warm-season, long-term observations during the warm season are needed, yet is rather limited.

In this work, we conducted one HONO observation in an urban site of Beijing, the time was from June to October 2021, covering the whole summer and part of autumn. According to the Technical Regulation on Ambient Air Quality Index in China, only one day of moderate pollution ($PM_{2.5}$, in October) and no more than four days of light pollution (ozone) per month were included, so we analysed the observation data on a monthly basis. The atmospheric levels and variations of HONO and related species during each month were analysed and compared. The impacts of HONO on atmospheric oxidant capacity in each month were also assessed.

2 Methods

2.1 Observation site and instruments

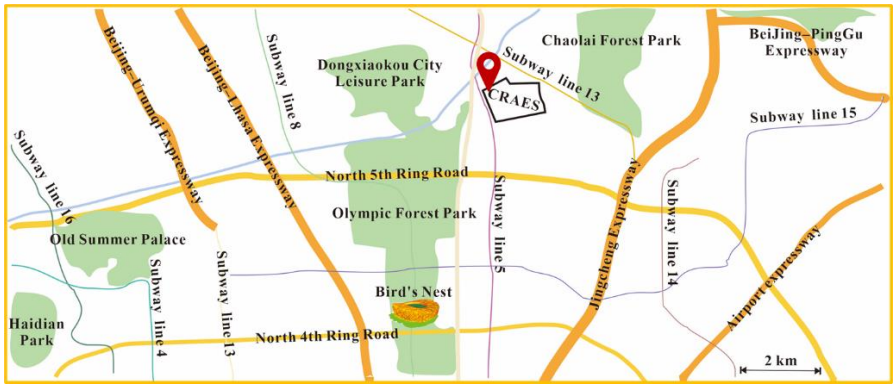


Figure 1: Location of the observation site in this work.

The observation campaign was conducted from June 18th, 2021 to October 25th, 2021. The observation site was located at Chinese Research Academy of Environmental Sciences (CRAES, 40°04´N, 116°42´E), in the north of Chaoyang District, an urban site (Ren et al., 2022;Zhang et al., 2021a) in Beijing, China (Figure 1). Briefly, Chaoyang District was located at the eastern area of Beijing and was one of the six main urban districts (Dongcheng, Xicheng, Haidian, Chaoyang, Shijingshan, and Fengtai) of Beijing. This site was located about 2 km to the north of the North Fifth Road, approximately 0.3 km away from Beiyuan Road, with a high volume of traffic. And this site was located in a mixed-use commercial and residential area, with several shopping malls, residential areas, and office buildings nearby, and there were no obvious sources of industrial pollution. Thus, this site could be considered as an urban site.

HONO was measured with a water-based long-path absorption photometer (Chen et al., 2020), the potential interferences, e.g., hydrolysis of NO_2, was subtracted by deployed a dual-channel absorption system. Briefly, the main

structure of the instrument sampling unit is a double-channel stripping coil. In the first coil, almost all of the HONO and a small fraction of interfering species (e.g., NO_2, peroxyacetyl nitrate, NO_2^-) are absorbed by deionized water; while in the second channel, only a small fraction of interfering species is absorbed, which could be seen as the comparable conversion ratio in both the first and second channels. Therefore, the HONO concentration output by the instrument is the difference in concentration between the first and second channels. As to the soluble species such as HO_2NO_2, considering its little ambient concentration, especially in warm season, the interfering could be neglected. A set of commercial analysers (Thermo 42i, 43i, 48i, 49i, 5030i, USA) were used to measure the concentrations of NO_x, SO_2, CO, O_3, and $PM_{2.5}$ online. Due to the employment of a molybdenum NO_2-to-NO converter, the 42i analyzer might overestimate NO_2 concentration for the potential convertion of NO_z ($NO_z = NO_y - NO_x$. e.g., HONO, HNO_3, peroxyacetyl nitrate (PAN), and so on). Based on this, we conducted field observations of NO_2 from May 19th to 31st, 2024, using two devices with different measurement principles (Figure S1). The observation results showed that when the NO_2 concentration was above 7 ppb, there was no significant difference between the two devices. However, when it was below 7 ppb, the 42i values were significantly higher than those of the N500, with a corresponding slope of 1.14. Based on this data, we have adjusted all NO_2 values below 7 ppb during the observation period, as well as the corresponding analyses. The time resolution of the analysers above were 1min, and the detection limits were 0.4 ppbv, 0.5 ppbv, 0.04 ppmv, 1ppbv, and 0.5 μg/m^3, respectively. In order to ensure the accuracy of the data, routine maintenance was carried out. The meteorological parameters (temperature, T; relative humidity, RH; pressure, P; wind speed and direction, WS and WD) were obtained with an automatic weather station (MAWS301, Vaisala, Finland) with a time resolution of 1 hr. Mass concentrations of the inorganic compositions in $PM_{2.5}$ (NO_3^-, SO_4^{2-}, Cl^-) were detected with a Monitor for AeRosols and Gases in ambient Air (MARGA, Model ADI 2080, Applikon Analytical B.V., the Netherlands) with 1 hr resolution. Detailed descriptions of the instrument inlet design and the operating characteristics can be referred in previous studies (Wang et al., 2022).

2.2 Photolysis rate simulation and OH estimation

Photolysis frequencies of JNO_2 were measured by a filter radiometer (METCON, Germany) with a time resolution of 1 min. Photolysis rate constant of O_3, HONO, and other parameters were simulated according to the aerosol optical depth and solar zenith angle by the weather research and forecasting model coupled with chemistry (WRF-Chem, version 3.7.1), based on the TUV model (http://cprm.acom.ucar.edu/Models/TUV/InteractiveTUV/) (Zhang et al., 2019a). To reduce the imprecision of model simulation, the observed JNO_2 value was used to correct simulated results, i.e., $J(O^1D)$ and J(HONO).

The OH concentration was calculated with the following equation (Liu et al., 2019):

$$[OH] = a \times \left(\frac{J(O^1D)}{10^{-5}s^{-1}}\right)^b + c \quad (1)$$

where a = 4.2 × 10^6 cm^{-3}, b = 1, c= 2.2 × 10^5 cm^{-3} (Lin et al., 2022), these coefficients adopted here were from the OH studies in the Pearl River delta (PRD) and Beijing, China (Rohrer et al., 2014; Tan et al., 2017, 2018). The influence of the uncertainty of the coefficients was estimated (Liu et al., 2019), results showed that the errors of OH increased with the

increase of $J(O^1D)$, but the ratios of error to mean value of OH radicals were in an acceptable range of 0.37-0.55. According to the summarizing coefficients in different OH observation campaigns in the polluted areas of China (Liu et al., 2019), the comprehensive impact of reactants (e.g., VOCs and NOx) on OH could not compete with that of UV light to OH, the chemical environments of OH could be similar. The OH concentration calculated through this formula was within a reasonable range and would not subvert the relative conclusions in this study. Thus, this could be a reasonable way to derive OH concentration by the equation above.

3 Results and discussion

3.1 Observation data overview

3.1.1 Variations of meteorological parameters during observation period

Figure S2 shows the time series of meteorological parameters including RH, T, WS, WD, and JNO_2 from June 18th, 2021 to October 25th, 2021. During the observations, the temperature ranged from 3.1-37 ℃ with an average of 23 ℃, and the RH ranged from 7.1%-100% with an average of 59%. The average wind speed during the observation was 1.1 m/sec, and the maximum wind speed was 5.20 m/sec. The average and monthly average values of T, RH, and WS are shown in Table S1. As shown in Figure S3 and Table S1, the temperature in June, July, and August was higher, 26-29 ℃, temperature begun to drop slightly in September, 22 ℃, in October, temperature dropped significantly, 13 ℃. Meanwhile, the solar radiation in September and October decreased as the sun moved south. The maximum value of $J(NO_2)$ during the observation was 8.2×10^{-3} s^{-1}, the values reached a maximum at noon (with high solar radiation) and decreased to zero at night. The average wind speed also slightly decreased in September and October. During the observation, June had the lowest RH and the maximum wind speed; and due to the increase in precipitation, July had the highest RH. For the daily variation of meteorological parameters, T and JNO_2 expressed the same variation pattern with O_3, that was increasing after sunrise and decreasing after sunset, as shown in Figure S3. While the RH showed the opposite pattern that was increasing during night and decreasing during the daytime. For the WS, it was higher from 8 to 20 o'clock in June, and for the rest of the observation period, WS begun to increase in the afternoon and subside after sunset.

3.1.2 Variations of pollutant species during observation period

Figure 2 shows the time series of basic parameters including HONO, NO_2, NO, CO, O_3, SO_2, PM_{10}, $PM_{2.5}$, and $HONO/NO_2$ from June 18th, 2021 to October 25th, 2021. The HONO concentration ranged from 0.05 ppb to 5.2 ppb, with an averaged value of 1.1 ppb (the entire observation period). The concentration of O_3 ranged from 1ppb to 227 ppb, with an averaged value of 72 ppb (the entire observation period). The concentrations of NO_2, NO, CO, SO_2, and $PM_{2.5}$ were 0.56-53 ppb, 0.01-210 ppb, 0.1-1.6 ppm, 1.3-4.6 ppb, and 1-181 $\mu g/m^3$, respectively, with average values (the entire observation period) of 10 ppb, 7.9 ppb, 0.56 ppm, 1.9 ppb, 19 $\mu g/m^3$, respectively. The average and monthly average concentrations of the basic

parameters are shown in Table 1. One haze episode (1 day) occurred across the observation period, the daily mass concentration of $PM_{2.5}$ was 117 μg/m^3, higher than the National Ambient Air Quality Standard (Class II: 75 μg/m^3). And for O_3, eight episodes (13 days) occurred across the observation period, with MDA8 O_3 higher than the Class II: 160 μg/m^3. Overall, the high HONO concentration was always accompanied by high concentration of NO_x (NO, NO_2) or aerosols ($PM_{2.5}$).

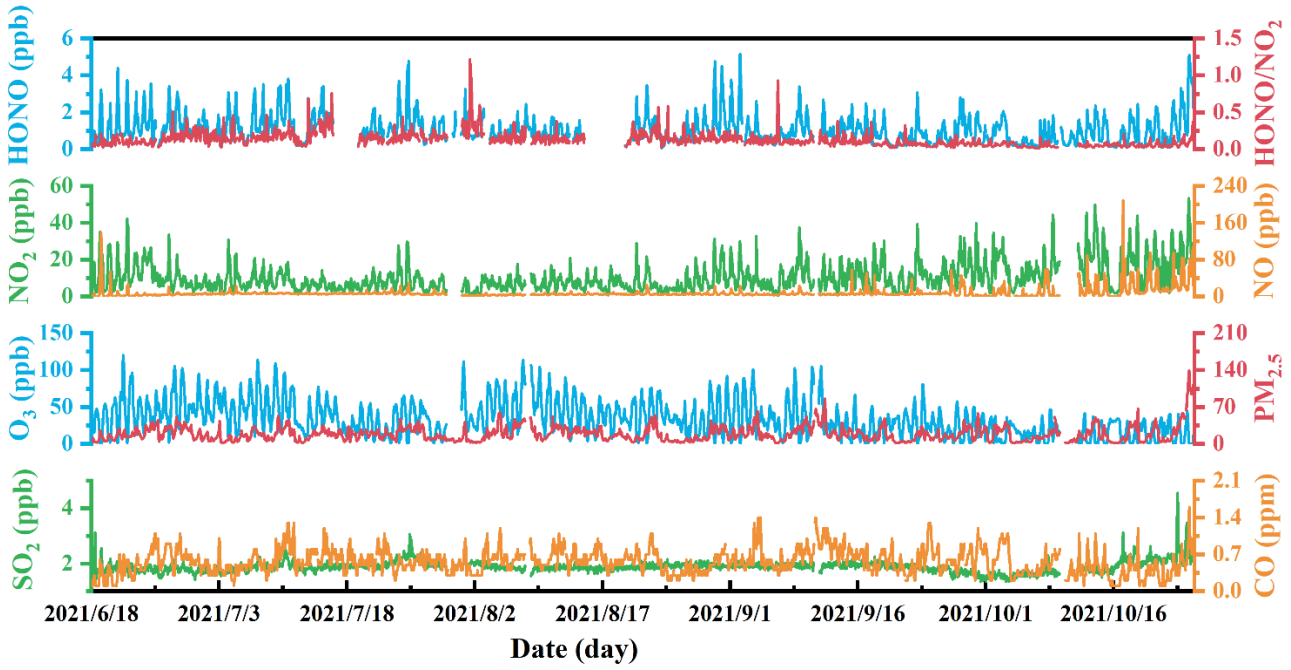


Figure 2: Temporal variations of hourly average $PM_{2.5}$, CO, O_3, SO_2, NO, HONO, NO_2, and HONO/NO_2 during the observation period.

Table 1. The average and monthly average concentration of HONO, NO_2, NO, CO, O_3, SO_2, $PM_{2.5}$, HONO/NO_2, and HONO/NO_2 from June to October during the observation period.

concentration		HONO (ppb)	NO_2 (ppb)	HONO/NO_2	NO (ppb)	CO (ppm)	O_3 (ppb)	SO_2 (ppb)	$PM_{2.5}$ (μg/m^3)
average (the entire observation period)		1.1	10	0.052	7.9	0.56	72	1.9	19
Jun.	average	1.3	12	0.051	5.7	0.52	88	1.8	20
	max	4.4	42	0.17	139	1.1	227	4	51
	min	0.14	2	0.0055	0.3	0.1	1	1.4	3
Jul.	average	1.3	7.5	0.072	6.6	0.56	78	1.9	17
	max	4.8	31	0.54	29	1.3	211	3.1	53
	min	0.11	1.1	0.0061	2.2	0.1	1	1.5	1
Aug.	average	1.0	7.1	0.079	4.8	0.57	87	1.9	19
	max	4.8	31	0.79	24	1.2	214	2.2	60
	min	0.052	0.62	0.0049	1.3	0.2	10	1.5	2
Sep.	average	0.96	11	0.035	6.7	0.65	68	1.9	19

	max	5.2	40	0.19	57	1.4	210	2.3	86
	min	0.078	0.56	0.0042	0.39	0.2	9	1.3	1
Oct.	average	0.89	17	0.025	17	0.46	40	1.9	23
	max	5.1	53	0.21	210	1.6	116	4.6	181
	min	0.066	1.7	0.0041	0.01	0.1	10	1.3	1

3.2 HONO observation comparison and pollution patterns

3.2.1 HONO observation comparison

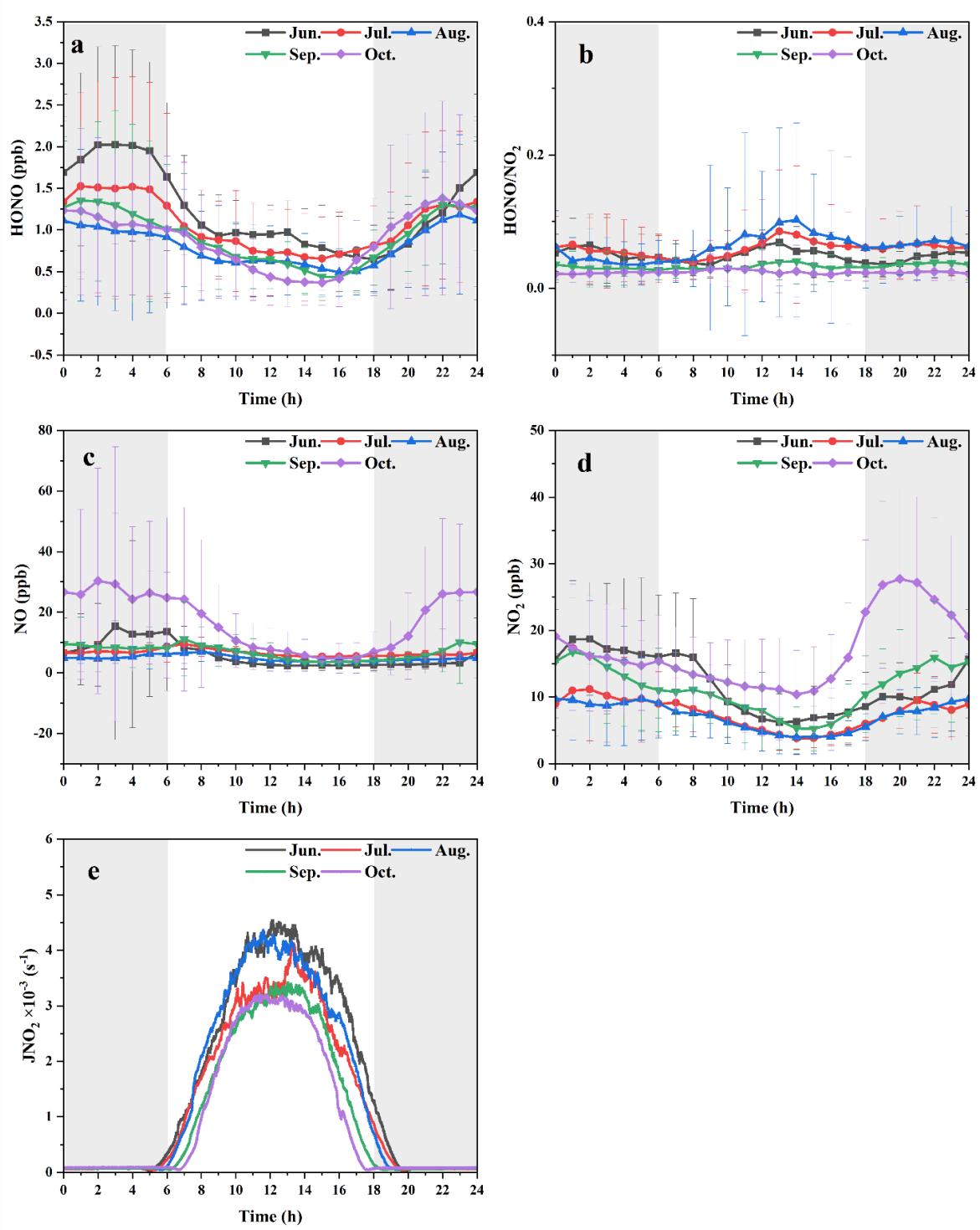
For comprehensive comparative analysis, a review of the HONO observations in Beijing was carried out in the past several years, and the results are shown in Table S2. Overall, the HONO measurement begun to increase since 2016 in Beijing, the time was mainly concentrated in winter (Dec., Jan., and Feb.), and most of which were pollution process analyses. In this work, the observation period was in summer and autumn. When the air quality was relatively poor in early years, $PM_{2.5}$ and HONO concentrations were both relatively high, now the air quality of Beijing was improved, both the concentration of $PM_{2.5}$ and HONO decreased. However, during the observation period, $PM_{2.5}$ concentration was low, HONO concentration was still relatively higher compared with other results performed in summer. According to previous studies (Murthy et al., 2020;Du et al., 2013), the narrowing of mixing layer could result in the accumulation of pollutants near the ground, while the increase of mixing layer height (MLH) favoured the dilution of pollutants. In general, the MLH was low in winter and high in summer. And the photochemistry was quite active in summer because of the strong solar radiation, in this case, HONO tended to undergo photolysis. However, our observations showed that HONO concentration in summer was comparable to that in winter and spring, and higher than that in autumn. Wang et al. (2023a) also found that in warm season, the $PM_{2.5}$ and MDA8 O_3 increased along with the development of MLH (MLH< 1200 m), they analysed that the enhanced secondary chemical formation and increased atmospheric oxidant capacity could explain this phenomenon. Based on this, we discussed the HONO sources in the following sections.

3.2.2 HONO variation patterns

The average diurnal variation of the pollutants during the whole observation period and the averaged values in each month are shown in Figure S4 and Figure 3. It can be seen that the daily averaged pattern of pollutant HONO is that it decreased after sunrise and increased after sunset, this variation pattern was similar to previous studies (Lin et al., 2022;Lian et al., 2022;Zhang et al., 2019a;Zhang et al., 2023b;Zhang et al., 2022). This trend was the same as NO_2. NO, $PM_{2.5}$, and CO, that was, the overall was relatively stable, and it decreased slightly during the daytime. The diurnal variation of SO_2 was not large, and the overall concentration was very low, but it had a slightly increase during the daytime. The variation of O_3 showed the opposite trend, i.e., its concentration increased after sunrise, peaked in the afternoon and decreased at night. The rapid decrease of HONO in daytime was caused by rapid photolysis and the increase of boundary layer height. The ratio of HONO/NO_2 is often used to characterized the heterogeneous reaction of NO_2 to form HONO (Yang et al., 2021a;El Zein et al., 2013;Romanias et al., 2012). At night, the HONO/NO_2 ratio was similar to that of HONO, but the ratio increased

obviously during the daytime, especially in summer (Jun., Jul., Aug.), and in summer, the light intensity was very strong, as revealed in Figure 3b and 3e. This phenomenon indicated that HONO might have other potential sources related to the solar radiation, e.g., the conversation of NO_2 to HONO or nitrate photolysis.

And when HONO was analysed in months, the characteristics of each month were different. For the HONO/NO_2 ratio in Figure 3b, August, July, June, and September were the months with a significant increase in the noon period, and there was no such phenomenon in October. However, it was important to note that the NO and NO_2 concentration in October were the highest in the entire observation period compared to the low HONO concentration. The NO and NO_2 concentrations in June were not high, but the HONO concentration was the highest. The phenomenon could not be explained by the well-known sources of HONO (Xuan et al., 2023).



200 **Figure 3. Diurnal variations in (a) HONO, (b) HONO/NO_2, (c) NO, (d) NO_2, and (e) JNO_2 in each month. The gray shading areas indicate nighttime, 18:00-06:00 LT.**

3.3 Nocturnal HONO sources and formation

3.3.1 Direct emission of HONO

Previous studies showed that the primary emission sources of HONO included biomass burning and vehicles as well as soil emissions (Nie et al., 2015;Su et al., 2011). In this study, soil emission was a negligible source of HONO, since the observation site was located in an urban area, the surrounding soil was not used for agriculture, which greatly reduced HONO emission caused by fertilization process (Su et al., 2011). Except organic compounds (Simoneit, 2002), CO in the gas phase (Andreae, 2019) and potassium ions (K^+) in the aerosol phase (Xinghua et al., 2007) were well recognized inorganic tracers of biomass burning. Many CO sources other than biomass burning, such as industry and traffic, could contribute significantly to the CO loading. Apart from biomass burning emissions, there were no other significant sources of K^+ during the measurement. Therefore, K^+ was a suitable tracer of biomass burning. According to studies on the influence of biomass burning on HONO chemistry (Nie et al., 2015), when K^+ concentration is higher than 2 μg m^{-3} and the ratio of K^+ to $PM_{2.5}$ is larger than 0.02, the plumes are defined as biomass burning samples. While the samples with K^+ concentrations lower than 2 μg m^{-3} and a ratio of K^+ to $PM_{2.5}$ smaller than 0.02 are categorized as non-biomass burning samples. The average K^+ levels during the five months were 0.14, 0.11, 0.11, 0.15, and 0.13 μg/m^3, respectively, lower than 2 μg/m^3 (Nie et al., 2015), which indicated that biomass burning had little effect on this observation site. Hence, only vehicle emission was considered in this study.

The HONO/NO_x ratio was used to derive the emission factor of vehicles in fresh plumes (Kurtenbach et al., 2001). Criteria followed by the fresh plumes were (Yun et al., 2017):

(a) $\triangle NO/\triangle NO_x > 0.9$

(b) good correlation between NO_x and HONO ($R^2 > 0.7$)

(c) short duration of plumes < 1 h

(d) positive correlation between CO and NOx

(e) no precipitation

(f) global radiation < 10 W/m^2, or $JNO_2 < 0.25\times10^{-3}$ s^{-1}

A total of 6 cases met the criteria mentioned above and the details were summarized in Table 2. The mean $\triangle NO/\triangle NO_x$ ratio of the selected fresh plumes was (97±4.4) %, which indicated that the chosen air masses were considered to be truly fresh. The linear slope of HONO with NO_x were used as the emission factors of HONO. The correlation coefficients (R^2) between HONO and NO_x varied among the cases due to the unavoidably mixing with other air masses, and the range was from 0.72 to 0.93. The obtained $\triangle HONO/\triangle NO_x$ ratios were from 0.32% to 2.49%, with an average value of (1.7± 0.74) %. Thus, a mean $\triangle HONO/\triangle NO_x$ value of 0.017 was used as the emission factor (EF) in this work. The $\triangle HONO/\triangle NO_x$ values obtained in urban area of Beijing in previous studies were also summarized in Table S2, the EF reported so far was concentrated in the range of 0.003-0.013, which was slightly lower than the EF in this work. The vehicle engine types,

catalytic converters use, and fuels could affect the emission factors of vehicles (Kurtenbach et al., 2001). According to Kessler and Platt (1984), diesel engines had a higher HONO/NO_x ratio than gasoline engines. In our study, the higher HONO/NO_x value possibly due to that the observation site was located outside the fifth ring road, and more heavy-duty diesel vehicles passed by on the surrounding road at night (regulations of the Public Security Traffic Management Bureau of the Beijing Municipal Public Security Bureau, i.e., from 6 a.m. to 11 p.m. every day, trucks are prohibited from passing on the roads within the Fifth Ring Road (exclusive), and trucks with an approved load weight of more than 8 tons (inclusive) are prohibited on the main road of the Fifth Ring Road). Assuming that NO_x mainly arose from vehicle emissions, the mean $\triangle$HONO/$\triangle NO_x$ value of 0.017 was adopted to estimate the vehicle emissions P_{emis} (ppb/h) contribution to the HONO concentration (this factor may lead to an overestimation of the P_{emis} at daytime):

$$P_{emis} = NO_x \times EF \quad (2)$$

Then the concentration of HONO in air that is not due to direct vehicular emissions (the corrected HONO concentration, $HONO_{corr}$) can be obtained from the following equation:

$$HONO_{corr} = HONO - P_{emis} \quad (3)$$

Table 2. Emission ratios ($\triangle$HONO/$\triangle$NOx) of fresh vehicle plumes.

Date (yyyy/mm/dd)	Time	$\triangle NO/\triangle NO_x$		$\triangle HONO/\triangle NO_x$	
		Slope (%)	R^2	Slope (%)	R^2
2021/6/21	2:25-3:15	99	1	2.5	0.73
2021/8/31	2:20-2:45	93	0.99	2.2	0.76
2023/9/15	3:30-4:20	104	0.98	2.1	0.83
2023/9/22	5:20-5:50	96	0.97	2.0	0.85
2023/10/3	0:40-0:55	94	0.99	1.2	0.93
2023/10/8	4:35-5:25	94	0.99	0.32	0.79

3.3.2 Nighttime heterogeneous conversion of NO_2

Heterogeneous conversion of NO_2 on ground or aerosol surface has been recognized as an important HONO source (Finlayson-Pitts et al., 2003;Liu et al., 2020). Nighttime $HONO_{het\text{-}night}$ concentration could be estimated from the heterogeneous reaction (R1, the mechanism of heterogeneous formation of HONO, and this was first order in NO_2 and H_2O (Alicke et al., 2002), and the conversion frequency of HONO ($k_{HONO,het\text{-}night}$) could be expressed as Equation 6. We determined the HONO formation by assuming a linear increase of its mixing ratio during a time interval (t_2-t_1). Since the mechanism summarized in R1 was first order in NO_2, the HONO formation was proportional to the NO_2 concentration. The conversion frequency was also assumed to be independent of gas phase water (Kleffmann et al., 1998), the average nighttime conversion frequency was determined by Equation 4,5, and 6. In order to eliminate the influence of direct emission and diffusion, CO was chosen as the reference species used for normalization:

$$2NO_2 + H_2O \xrightarrow{\text{ground,aerosol surface}} HONO + HNO_3 \quad (R1)$$

$$k^0_{HONO} = \frac{[HONO_{corr,night}]_{t2} - [HONO_{corr,night}]_{t1}}{(t_2 - t_1)\overline{[NO_2]}} \quad (4)$$

$$k_{HONO}^{X} = \frac{(\frac{[HONO_{corr,night}]_{t2}}{[X]_{t2}} - \frac{[HONO_{corr,night}]_{t1}}{X_{t1}})\overline{[X]}}{0.5(t_2-t_1)(\frac{[NO_2]_{t2}}{[X]_{t2}}+\frac{[NO_2]_{t1}}{[X]_{t1}})\overline{[X]}} = \frac{2(\frac{[HONO_{corr,night}]_{t2}}{[X]_{t2}} - \frac{[HONO_{corr,night}]_{t1}}{X_{t1}})}{(t_2-t_1)(\frac{[NO_2]_{t2}}{[X]_{t2}}+\frac{[NO_2]_{t1}}{[X]_{t1}})} \quad (5)$$

$$k_{HONO,het-night} = \frac{1}{2}(k_{HONO}^{0} + k_{HONO}^{CO}) \quad (6)$$

where $\overline{[NO_2]}$ was the mean value of NO_2 concentration between time t_2 and t_1, k_{HONO}^{0} was the conversion frequency which was not scaled, and k_{HONO}^{X} was the conversion frequency scaled with reference gases X (CO). Then the NO_2 to HONO conversion rate (k_{HONO}) was calculated by the combination of k_{HONO}^{0} (not scaled k_{HONO}) and k_{HONO}^{CO} (CO scaled k_{HONO}), which could reduce the impact of uncertainties in diffusion process and emissions on the conversion rate.

Table 3. The conversion frequency k_{HONO} and $k_{HONO}[NO_2]$ in each month during the observation period.

	June	July	August	September	October
$k_{HONO,het-night}$ (hr^{-1})	0.011±0.003	0.01±0.002	0.0093±0.0015	0.0081±0.0006	0.0016±0.0002
$k_{HONO,het-night}[NO_2]$ (ppb/hr)	0.15±0.02	0.089±0.6%	0.079±0.004%	0.11±0.01	0.032±0.001

The averaged values of $k_{HONO,het-night}$ during the observation period were 0.011 hr^{-1}, 0.01 hr^{-1}, 0.0093% hr^{-1}, 0.0081 hr^{-1}, and 0.0016 hr^{-1}, respectively, for June, July, August, September, and October, with 0.008 hr^{-1} on average. The averaged value was slightly higher than that reported by Xuan et al. (2023) and Jia et al. (2020), 0.0073 hr^{-1} and 0.0078 $hr^{-1}$from August to September, 2018. The varied values of k_{HONO} in each month indicated the different environmental conditions in each month, e.g., surface features, aerosol concentrations (Su et al., 2008). As shown in Table 3, June had the highest $k_{HONO,het-night}[NO_2]$ this indicated that the heterogeneous conversion from NO_2 was more important for HONO formation at night in June.

In general, the importance of the two generation pathways of nocturnal HONO might change due to the time and environmental factors. The North China has four distinct seasons, temperature and relative humidity varies with the seasons, pollutants in the gas phase and particle phase in the environment can also be affected, and the factors of observation location and observation time should be taken into account when evaluating the relative contribution of the generation pathways to HONO.

3.4 HONO daytime budget

3.4.1 Budget analysis of HONO

According to the source and sink pathways of HONO mentioned on introduction section, the sources of HONO on the daytime (10:00-15:00 LT) include: (1) direct emission of HONO (P_{emis}), (2) homogeneous reaction of NO with OH ($P_{OH+NO}=k_{OH+NO}[OH][NO]$), (3) the unknown sources during the daytime ($P_{unknown}$) (4) the vertical (T_v) and horizontal (T_h) transport processes of HONO. According to related observations (Wong et al., 2011; Wong et al., 2012; Wong et al., 2013; Pinto et al., 2014; Stutz et al., 2002; Wang et al., 2006; VandenBoer et al., 2013; Young et al., 2012), photolytic HONO formation at the ground is the major formation pathway in the lowest 20 m, while a combination of gas-phase, photolytic formation on aerosol, and vertical transport is responsible for daytime HONO between 200-300 meters above the ground. In

our work, the measurement was conducted on the rooftop of one building, about eight meters above the ground. As vertical exchange is unknown since the data to calculate its effect on HONO measured at 8 m is not available. Therefore, all subsequent analysis relies on the assumption that vertical exchange is unimportant, but this assumption represents an uncertainty that is not easily quantified; the sinks of HONO on the daytime include: (1) dry deposition of HONO ($L_{dep}=\frac{V_{HONO}}{H}[HONO]$), (2) photolysis of HONO ($L_{phot} = J_{HONO}[HONO]$), (3) reaction of OH with HONO ($L_{OH+HONO} = k_{OH+HONO}[HONO][OH]$).

The budget of HONO can be calculated by the following equation (8), (9), and (10):

$$\frac{dHONO}{dt} = (P_{emis} + P_{OH+NO} + P_{unknown}) - (L_{dep} + L_{phot} + L_{OH+HONO}) \quad (8)$$

$$P_{unknown} = \frac{dHONO}{dt} + L_{dep} + L_{phot} + L_{OH+HONO} - P_{emis} - P_{OH+NO} \quad (9)$$

$$P_{unkown} = \frac{\Delta HONO}{\Delta t} + k_{OH+HONO}[OH][HONO] + J_{HONO}[HONO] + \frac{V_{HONO}}{H}[HONO] - k_{OH+NO}[OH][NO] - P_{emis} \quad (10)$$

where $\frac{dHONO}{dt}$ represents the difference between HONO sources and sinks; $\frac{\Delta HONO}{\Delta t}$ was the observed change of HONO, the rate constants of k_{NO+OH} and $k_{HONO+OH}$ at 298k were 9.8×10^{-12} and 6.0×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively (Liu et al., 2021a). A value of V_{HONO} = 1.6 cm/s was adopted here for the deposition rate of HONO (Zhang et al., 2019b), the value of H = 200 m was used here as the mixing layer height (Hu et al., 2022). The OH concentration and J_{HONO} were calculated with the method mentioned in section 2.2. According to the model simulation results, the averaged J_{HONO} values were in the range of 0.78×10^{-3} - 1.4×10^{-3} s^{-1}. The daytime hourly averaged values of OH concentration in the five months were in the ranges of 2.9×10^{6}-8.9×10^{6} molecules/cm^3.

Figure 4 illustrated the details production/loss rates and proportion of HONO during the observation period. And Table S3 showed the averaged production/loss rates of HONO around noontime (10:00-15:00 LT). The dominant loss pathway of HONO during the five months was the photodecomposition (L_{phot}), the averaged values of L_{phot} were 1.1-3.9 ppb/hr around noontime. The following loss pathway of HONO was dry deposition (L_{dep}), the averaged values of L_{dep} were 0.13-0.27 ppb/hr around noontime. The loss pathway with the least contribution was the reaction of OH with HONO ($L_{OH+HONO}$), the averaged values of $L_{OH+HONO}$ were 0.029-0.15 ppb/hr at the same time. For the production pathways of HONO around noontime, the averaged values of homogeneous reaction rate between NO and OH (P_{OH+NO}) were 0.64-1.5 ppb/hr. The averaged values of P_{emis} were 0.16-0.33 ppb/hr. For the high value of P_{emis} in October, the possible reasons maybe that the corresponding diffusion conditions were weakened due to the decrease in wind speed, and the change of epidemic control policies in this area in October resulted in the increase of the traffic emissions. The averaged values of $P_{unknown}$ were 0.29-2.7 ppb/hr, the contribution of which to the production of HONO were 78% (June), 55% (July), 64% (August), 68% (September), and 30% (October), respectively. In summary, photodecomposition was the largest removal pathway around noontime during the whole observation period; $P_{unknown}$ contributed the most to the production of HONO in June, July, August, and

September, homogeneous reaction of NO and OH dominated the HONO production in October at daytime; June had the highest $P_{unknown}$, and October had the lowest $P_{unknown}$.

The obtained average $P_{unknown}$ values in Summer (from June to August), 2.3 ppb/hr, was at the middle level of those reported literatures in urban areas, as shown in Table 4. The $P_{unknown}$ values in Autumn (from September to October) (1.0 ppb/hr) was at the lower-middle level of those reported literatures in urban aeras.

Table 4. The $P_{unknown}$ values in this work and reported literatures.

Date		value (ppb/h)	location	literatures
Summer	18 August to 16 September, 2018	0.49	Beijing	Xuan et al., 2023
	June to July, 2019	0.59	Beijing	Li et al., 2021
	24 July to 6 August, 2015	0.75	Xi'an	Huang et al., 2017
	1 June to 31 August, 2018	0.98	Nanjing	Liu et al., 2019
	8-20 March, 2005	1.7	Santiago	Elshorbany et al., 2009
	June to August, 2021	2.3	Beijing	This work
	25 May to 15 July, 2018	2.1	Beijing	Liu et al., 2021a
	1 June to 31 August, 2016	3.0	Jinan	Li et al., 2018
	20 June to 25 July, 2016	3.8	Beijing	Wang et al., 2017a
	August, 2018	4.5	Xiamen	Hu et al., 2022
Autumn	27 September to 9 November, 2018	0.65	Guangzhou	Yu et al., 2022b
	September to October, 2021	1.1	Beijing	This work
	October, 2018	2.1	Xiamen	Hu et al., 2022
	23 August to 17 September, 2018	2.3	Beijing	Jia et al., 2020
	22 September to 21 October, 2015	3.1	Beijing	Wang et al., 2017a

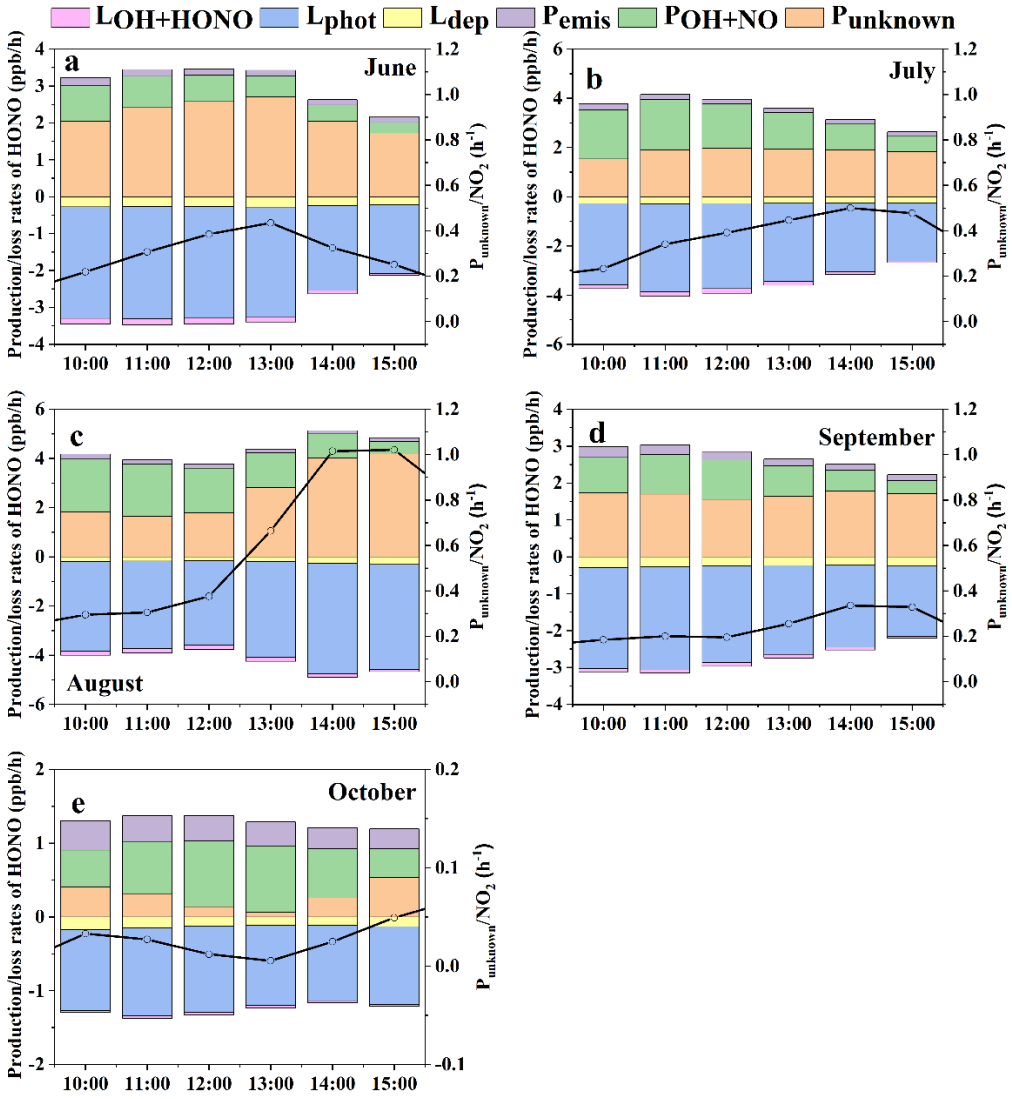


Figure 4. Daytime HONO budget in average production (P_{emis}, P_{NO+OH}, $P_{unknown}$) and loss rates ($L_{OH+HONO}$, L_{phot}, L_{dep}) during the five months.

3.4.2 Possible unknown source at daytime

Based on the assumption that nighttime heterogeneous conversion of NO_2 continued in the same way at the daytime, the nighttime heterogeneous production of HONO was adopted here, and $P_{het} = k_{HONO}[NO_2]$ (Alicke, 2002;Sörgel et al., 2011). Dark heterogeneous formation accounted for 6.5% (June), 4.9% (July), 2.9% (August), 6.5% (September), and 11% (October) of missing sources of HONO at daytime, respectively, which was almost negligible at daytime. And the average value of $P_{unknown}$ normalized by NO_2 at daytime (10:00-15:00 LT) was 0.025-0.61 h^{-1}, as shown in Table S3, much greater

than the conversion rates at nighttime. This phenomenon implied that $P_{unknown}$ could not be explained by the nocturnal mechanism of NO_2 to HONO.

According to the reported possible HONO sources in literatures (Zhang et al., 2023c;Zhang et al., 2022;Lian et al., 2022), light-induced heterogeneous conversion from NO_2 to HONO and photolysis of nitrate were responsible for the $P_{unknown}$, solar illumination and relative humidity were the two most frequently considered meteorological factors. Thus, a correlation analysis was performed to explore the potential unknown sources of HONO at daytime, and the details are shown in Table S4.

Wang et al. (2017a) analysed the data of Beijing from 20 June to 25 July 2016 (summer) and found that, compared to JNO_2 or RH alone, the correlation between $P_{unknown}$ and product of JNO_2 and RH was good. Based on this phenomenon, it was thought that photolytic and heterogeneous reaction occurring upon wet surface were important unknown sources of HONO. In our work, good correlation between $P_{unknown}$ and product of JNO_2 and RH was found in June. However, this phenomenon was not evident in other four months. The phenomenon was not evident in four of the five months, this showed that in this observation there was not strong evidence for this conclusion. As shown in Table S4, June had the lowest RH and the highest JNO_2 value, the other four months had relative higher RH (due to the precipitation) and lower JNO_2 value. This phenomenon may be closely related to meteorological conditions and requires further research for validation.

In August and September, it could be seen that low NO_2 and $PM_{2.5}$ conditions could lead to high $P_{unknown}$, corresponding to high JNO_2 value and relatively low RH (20-40%). This phenomenon suggested that there were other possible unknown sources of HONO, and this might be due to the light-enhancing effect of NO_2 on non-aerosol surfaces.

Through heterogeneous photochemical simulation experiments, Wingen et al. (2008) found that an enhanced NO_2 yield was observed as the chloride to nitrate ratio increased. Jin et al. (2022) performed the nitrate photolysis experiments with a flow tube reactor, and found that surprising yields of HONO and NO were formed during the photolysis experiment of NH_4NO_3 in the presence of halogen ions (Cl^-, Br^-, I^-), this phenomenon indicated the important role of halogen ions in nitrate photolysis process. Thus, we analysed the correlation between nitrate and $P_{unknown}$ in the presence of Cl^- ion. As shown in Table S4, the correlation between $P_{unknown}$ and the corresponding factors was as follows: $JNO_2 \times [NO_3^-] \times Cl^-$ ($R = 0.46$, $P<0.05$) $>$ $JNO_2 \times [NO_3^-]$ ($R = 0.29$, $P<0.05$) in July; $JNO_2 \times [NO_3^-] \times RH \times Cl^-$ ($R = 0.44$, $P<0.05$) $>$ $JNO_2 \times [NO_3^-] \times RH$ ($R = 0.30$, $P<0.05$) in July. Bao et al. (2018) found that a large amount of HONO and NO_x were formed during the photolysis experiment of nitrate in the presence of sulfate. Significant positive correlations also occurred in our observations in July: $JNO_2 \times [NO_3^-] \times SO_4^{2-}$ ($R = 0.32$, $P<0.05$) $>$ $JNO_2 \times [NO_3^-]$ ($R = 0.29$, $P<0.05$); $JNO_2 \times [NO_3^-] \times RH \times SO_4^{2-}$ ($R = 0.33$, $P<0.05$) $>$ $JNO_2 \times [NO_3^-] \times RH$ ($R = 0.30$, $P<0.05$). Yang et al. (2018) and Ye et al. (2019) found that the presence of organic components significantly enhanced the denitrification rate of nitrate. In this work, organic carbon (OC) was used as a proxy for organic components, and the correlation was analysed. As shown in Table S4, the enhancement of the correlation between $P_{unknown}$ and NO_3^- in the presence of OC was observed, $JNO_2 \times [NO_3^-] \times OC$ ($R = 0.55$, $P<0.05$) $>$ $JNO_2 \times [NO_3^-]$

(R = 0.48, P<0.05) in June. However, the phenomenon above were not evident in four of the five months, this showed that in this observation there was not strong evidence for these conclusions, but that they could contribute based on prior literatures.

3.4.3 OH production rate at daytime

As HONO was the efficient source of OH radical at daytime (Zhang et al., 2023c;Yu et al., 2022b), the OH production rate from HONO ($P_{OH\text{-}HONO}$) at the CRAES observation site was calculated in this work. As the formaldehyde was not measured in this work, which was a large and known HO_x source in urban areas, thus the analysis here was not a full HO_x buddget.

Figure 5 showed that the OH production rate from HONO usually occurred before noontime, and this was caused by the existing HONO and its photolysis, this phenomenon was obvious in July, September, and October. And for $P_{OH\text{-}O3}$ (the production rate of OH radical via O_3 photolysis to O1D followed by reaction with water vapor), the highest value was around noontime, which coincided with $J(O^1D)$ trend, this phenomenon was obvious in June, July, and August. In September and October (autumn), the highest value of $P_{OH\text{-}O3}$ occurred a little later after noontime. The average $P_{OH\text{-}HONO}$ during 8:00-16:00 LT was 2.7 ppb/h (June), 2.9 ppb/h (July), 2.0 ppb/h (August), 2.3 ppb/h (September), and 0.93 ppb/h (October), respectively; And the average $P_{OH\text{-}O3}$ during 8:00-16:00 LT was 0.45 ppb/h (June), 0.82 ppb/h (July), 0.51 ppb/h (August), 0.33 ppb/h (September), and 0.048 ppb/h (October), respectively; the contribution of HONO to OH was significantly greater than that of ozone. The important role of HONO to OH in the atmospheric oxidizing capacity should benefit the production of photochemical ozone (Xuan et al., 2023;Jia et al., 2023;Zhang et al., 2023b;Zhang et al., 2022), the formation of new particles (Stolzenburg et al., 2023), and the formation of secondary aerosols (Zhang et al., 2023c;Xuan et al., 2023;Liu et al., 2021a).

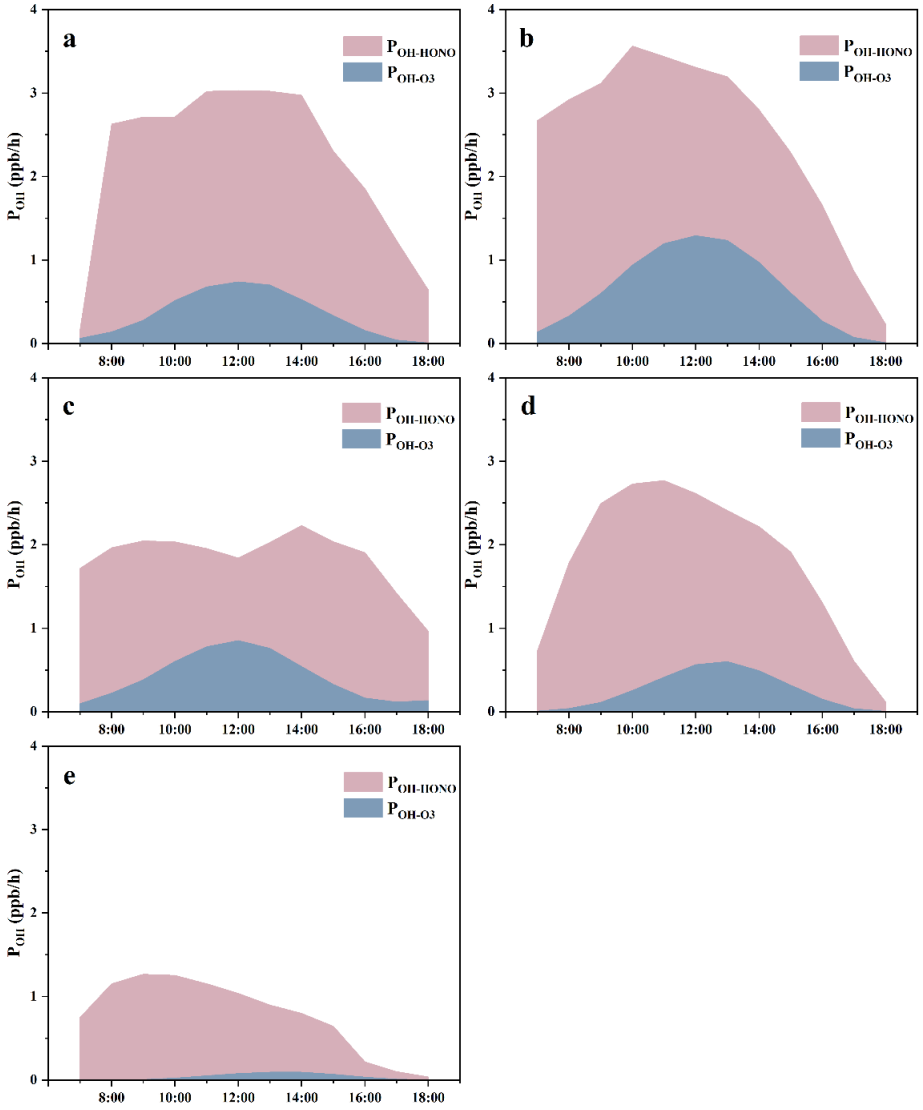


Figure 5. Averaged OH production rates from photolysis of HONO and ozone in (a) June, (b) July, (c) August, (d) September, and (d) October.

3.5 The correlations between HONO, $PM_{2.5}$, and O_3

In view of the importance of HONO to atmospheric oxidizing capacity (Zhong et al., 2023;Zhang et al., 2023b;Song et al., 2023), the correlations between HONO, $PM_{2.5}$, and O_3 were analysed. According to the Technical Regulation on Ambient Air Quality Index (on trial) in China (633—2012, 2012), $PM_{2.5}$ concentrations were divided into three zones: ≤ 35 μg/m^3, 35-75 μg/m^3, and ≥ 75 μg/m^3; and analysed at nighttime and daytime, respectively.

As shown in Figure 6, $PM_{2.5}$ concentrations were positively correlated with HONO, i.e., the increase of $PM_{2.5}$ pollution was accompanied by the increase of HONO concentration during the daytime. At night, except in September, the same

pattern was presented. One possible explanation of this phenomenon was that the increase in particle pollution in summer and autumn might lead to the formation of HONO and an increase in its concentration. Another possible explanation was that high HONO concentrations could lead to higher oxidative capacity and therefore higher rates of aerosol formation. There was also a possible explanation as both $PM_{2.5}$ and HONO were stem from the same sources (i.e., their concentrations would both increase during pollution events). However, when it came to ozone, we could see a different phenomenon. In June and July, ozone showed a decreasing trend as particle and HONO concentrations increased during the daytime, but when at night, ozone concentrations tend to increase. In August and September, ozone showed an increasing trend as particle and HONO concentration increased both during the daytime and nighttime. In October, ozone showed an increasing trend at daytime, but a decreasing trend at night. Wang et al. (2017b) summarized the ozone abundance and its relationship to chemical processes and atmospheric dynamics in China, the ozone formation and concentration could be affected by various factors, including precursors, meteorological factors, and regional transport, et al., the formation of OH radical by HONO photolysis was a pathway involved in the RO_x and NO_x cycle of ozone formation, ozone was not directly related to HONO.

Wang et al. (2023a) analysed the relationships between ozone, $PM_{2.5}$, and mixing layer height in warm season, and found that the enhanced atmospheric oxidant capacity could promote the secondary transformation of particles, and weakened the dilution effect of mixing layer height rise on pollutants. The contribution of observed HONO to atmospheric oxidant capacity exceeded that of ozone, so it was necessary to pay more attention to the sources of HONO in warm season.

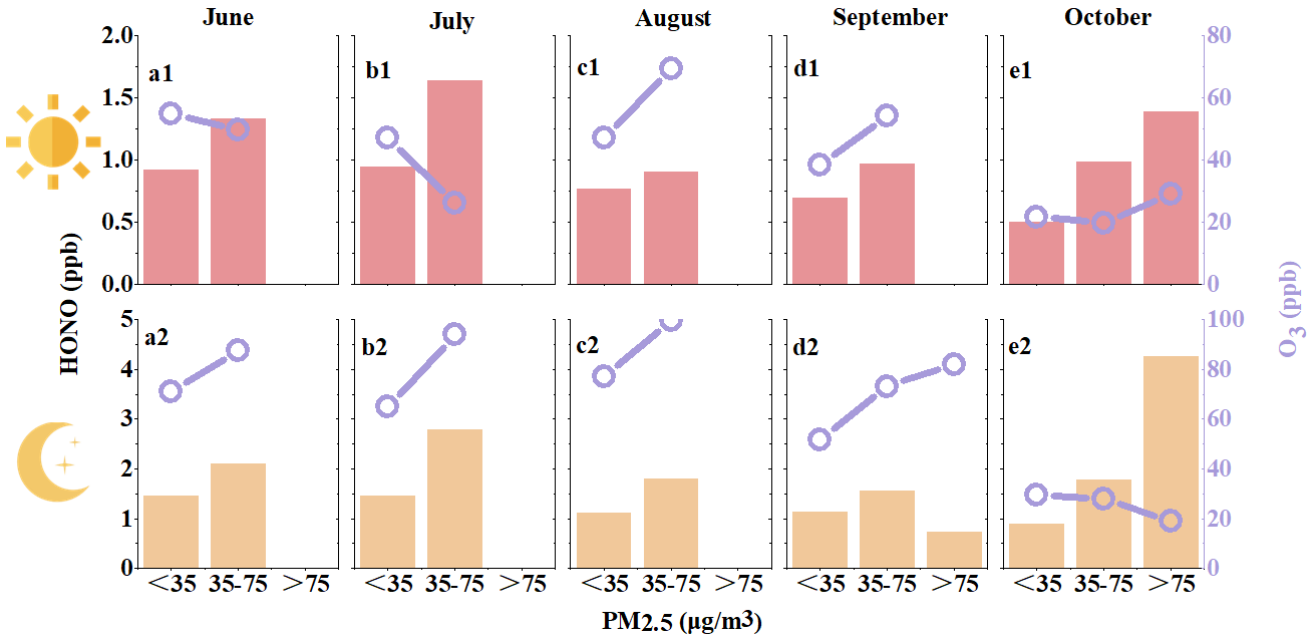


Figure 6. Distributions of HONO and O_3 mean concentrations under different $PM_{2.5}$ pollution conditions. The upper panel was the daytime average value (7:00-18:00 LT), and the bottom panel was the nighttime average value (19:00-6:00 LT).

4 Conclusions

Continuous field observation of HONO in warm seasons was conducted in an urban site of Beijing, from June to October 2021. The monthly average HONO concentration was in the range of 0.89-1.28 ppb, showing a larger contribution to OH radical relative to ozone at daytime, above three times as that of ozone in each month. Compared with previous field observations in the urban sites of Beijing, the contribution of vehicle emissions to HONO (0.017) was relatively high. The monthly nocturnal conversion rate of NO_2 to HONO was in the range of 0.0016-0.011 hr^{-1}, accounted for 2.9%-11% of missing sources of HONO at daytime; the average value of $P_{unknown}$ normalized by NO_2 at daytime (10:00-15:00 LT) was 0.025-0.61 hr^{-1}, much greater than the conversion rates at nighttime, which indicated that nocturnal heterogeneous conversion from NO_2 to HONO was almost negligible at daytime.

Based on the field observations in summer and winter, Liu et al. (2021b) evaluated the atmospheric oxidizing capacity in the megacity of Beijing, and found that the atmospheric oxidizing capacity showed a clear seasonal pattern, which was stronger in summer than that in winter. The dominant oxidant contributor to atmospheric oxidizing capacity at daytime was OH radical, and ozone was the second most important oxidant. Our work showed that in summer and autumn, the contribution of HONO to OH radical was significantly greater than that of ozone, this further illustrated the importance of HONO. As mentioned in Section 3.4.1, the contributions of $P_{unknown}$ to the production of HONO were 78% (June), 55% (July), 64% (August), 68% (September), and 30% (October), respectively. According to the OH production from HONO, the OH production rate from the missing HONO was also very important to atmospheric oxidation capacity. Thus, further investigation was required to figure out the source of HONO. In recent years, the concentration of atmospheric particulate matter in China decreased significantly, but the ozone concentration showed a fluctuating upward trend, the atmospheric oxidation capacity increased significantly, especially in the warm season. Given the contribution of HONO to atmospheric oxidation capacity, its sources should be studied in more detail.

Code and data availability. The data used in this study are available upon request from the corresponding author.

Author contributions. JLL and HL conceived and led the studies. JLL, CFL, HZ, WGW, and HL performed observation studies and data analysis. MML, YXY, YFS, CC, YCG, YSX, JG, and MFG discussed the results and commented on the paper. JLL prepared the article with contributions from all co-authors.

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

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