



Measurement report: Anthropogenic activities reduction suppresses HONO formation: Direct evidence for Secondary Pollution control

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Abstract. Nitrous acid (HONO) is a key precursor of atmospheric hydroxyl radicals (OH) and significantly influences the formation of secondary pollutants, making it essential for understanding and controlling air pollution. While many studies have focused on its formation mechanisms, few have explored the impact of anthropogenic activities variation on HONO formation. Therefore, we investigated the impact of anthropogenic activities variation on HONO formation based on a comprehensive observation conducted in urban Beijing during autumn and winter of 2022. During clean periods with a 53% drop in Traffic Performance Index, HONO, CO, and NO₂ levels decreased by 2–3 times compared to polluted periods and significantly lower than previously reported wintertime levels in Beijing. Source apportionment revealed that NO₂ heterogeneous reaction on ground was the dominant HONO source across all periods. Vehicle emissions contributed more to HONO during clean periods, suggesting that reduced anthropogenic activities has a stronger influence on secondary HONO formation. NO₃⁻ photolysis contributed more to HONO during polluted periods, due to higher NO₃⁻ fractions in PM_{2.5} under more polluted conditions. Despite including all known formation pathways in the model, unidentified HONO sources still remain. This is strongly associated with intense solar radiation and high OH concentrations at daytime, as well as elevated NH₃ concentrations at nighttime. Emission reduction simulations further revealed that a 50% NO_x reduction during polluted periods could lower HONO by up to 38.4%, directly demonstrating that reducing anthropogenic activities significantly suppresses HONO formation and provides a scientific basis for the development of air pollution control strategies.



1 Introduction

The worsening global environmental and public health challenges are largely driven by secondary pollution, primarily associated with haze and tropospheric ozone (O_3). This widespread issue poses substantial risks to both human health and food security (Huang et al., 2014; Wang et al., 2024; Achebak et al., 2024; Chen et al., 2024b; Li et al., 2019). Therefore, identifying the key processes controlling the formation of haze and O_3 pollution is critical for improving understanding and informing effective environmental management strategies at the global scale.

The hydroxyl (OH) radicals play a dominant role in secondary pollution (Wang et al., 2023; Tan et al., 2024). Previous studies have found that the photolysis of HONO not only serves as the "trigger" for daytime photochemical reactions in the early morning, but also acts as an important, and even primary source of OH radicals throughout the whole day (Kim et al., 2014; Xue et al., 2016). The more severe pollution, and the higher contribution of HONO to primary OH radicals (70–92 %) (Xue et al., 2020; Slater et al., 2020; Xuan et al., 2024). Due to its importance in atmospheric chemistry, the formation mechanisms of HONO have garnered widespread attention (Zhang et al., 2019a; Cui et al., 2018). HONO can be directly emitted into the atmosphere from primary sources, including fossil fuel combustion (Kurtenbach et al., 2001; Liao et al., 2021; Zhang et al., 2022a; Zhang et al., 2022b), biomass burning (Gu et al., 2020; Theys et al., 2020), and agricultural soils (Xue et al., 2024; Bao et al., 2022), all of which are closely related to anthropogenic activities. Secondary formation of HONO involves gas-phase reactions (Pagsberg et al., 1997; Slater et al., 2020), heterogeneous processes on surfaces (Chen et al., 2023; Yang et al., 2021; Wall and Harris, 2017; Zhang et al., 2023c), and photochemical processes (Ye et al., 2017; Jiang et al., 2024; Chen et al., 2024a). The precursors of these processes (e.g., NO, NO_2 , and NH_3) also predominantly originate from anthropogenic activities (Yu et al., 2021; Liu et al., 2019a). In summary, anthropogenic activities significantly impact HONO formation. Therefore, understanding how anthropogenic activities variations affect HONO formations and OH radicals is critical for evaluating the effectiveness of human emission controls and for formulating targeted emission reduction policies.

Policy adjustments and energy structure optimization can significantly affect the characteristics and sources of HONO, as well as its contribution to secondary pollution such as $PM_{2.5}$ and O_3 . As the capital of China, Beijing is one of the key areas of air pollution under the supervision of Ministry of Ecology and Environment of the People's Republic of China (Li et al., 2020). Over the past decade, Beijing had implemented various measures, including the Clean Air Action Plan in 2013 and the Three-Year Action Plan from 2018 to 2020, and had moved many heavy-polluting industries out of Beijing to control industrial pollution (Zhang et al., 2016; Chan and Yao, 2008). Additionally, the control of vehicle emissions and coal combustion in Beijing had been one of the key tasks (Zhang et al., 2016). With the implementation of these policies, $PM_{2.5}$ concentration had decreased rapidly, while O_3 concentration had increased year by year in Beijing. Moreover, despite the reduction in nitrogen oxides (NO_x) emissions, the nitrate (NO_3^-) concentration and its proportion in $PM_{2.5}$ had increased (Zong et al., 2022). The air pollution control focus had shifted from single $PM_{2.5}$ control to the simultaneous control of both $PM_{2.5}$ and O_3 (Liu et al., 2020; Ye et al., 2023). Stagnant meteorological conditions, such as low wind speeds and high



relative humidity, are key drivers of air pollution in autumn and winter. Previous studies have highlighted how such meteorological conditions facilitate the development of second pollutions in Beijing, with weak southerly winds often driving pollution from industrial regions (Guo et al., 2014; Zheng et al., 2015). In addition, direct anthropogenic emissions, particularly traffic emissions and coal combustions, also are crucial contributors to wintertime PM_{2.5} during haze events in northern Chinese cities (Guo et al., 2013; Shen et al., 2024). Thus, both meteorological stagnations and anthropogenic emissions are the primary drivers of secondary pollution formation in Beijing.

While previous studies have generally focused on HONO source and sink analysis (Xuan et al., 2024; Lin et al., 2022; Jia et al., 2020), limited research has explored the impact of anthropogenic activities variations on HONO formation and atmospheric oxidation under different pollution conditions. Hereby, we had conducted a field observation campaign in urban Beijing from 20 September to 23 December 2022, covering the autumn and winter seasons when O₃ and PM_{2.5} pollution frequently occurred. HONO and related pollutants (NO, NO₂, SO₂, CO, O₃, NH₃, NO₃⁻, PM_{2.5}, and PM₁₀), as well as meteorological parameters, were simultaneously measured. During this observations, stagnant meteorological conditions predominated, with low wind speeds and southerly winds. Therefore, the variations in concentration primarily reflect changes in local emissions caused by anthropogenic activities. It provided a unique opportunity to identify HONO sources and their potential impact to secondary pollution formation in urban Beijing, which has been rarely studies in the past. In addition, a box model coupled with the Regional Atmospheric Chemistry Mechanism version 2 (RACM2) was used to investigate the chemical budget of HONO under different pollution conditions and to quantify the impact of anthropogenic activities variations on HONO formation. In summary, through continuous field observations and model simulations, we provided direct evidence that reducing anthropogenic activities is crucial for controlling wintertime HONO formation in Beijing, providing a direct basis for formulating effective air pollution control strategies.

2 Experimental Methods

2.1 Measurement site

The measurement site in this study was on the third floor of NO.2 building at Institute of Chemistry, Chinese Academy of Sciences (ICCAS, 39.99° N, 116.32° E) in Beijing. It is a typical urban site with no obvious industrial or agricultural emission sources. This site is surrounded by dense buildings and main roads, including the North Fourth Ring Road about 500 m to the south of the site and Chengfu Road about 200 m to the north. Therefore, it is heavily influenced by vehicle emissions and anthropogenic activities. More details about the measurement site have been described by previous studies (Hou et al., 2016; Zhang et al., 2023b; Zhang et al., 2019b). The mixing ratios of atmospheric HONO, NH₃, NO, NO₂ and meteorological parameters were measured at ICCAS. In addition, mixing ratios of other trace gases (including O₃, CO and SO₂), PM_{2.5} and PM₁₀ were obtained at the Wanliu monitoring station of the Beijing Environmental Monitoring Station. The Wanliu monitoring station was just about 3 km away from our measurement site in this study, so the atmospheric environment at the two sites was also similar. In addition, photolysis frequencies (j_{O1D}, j_{NO2}, j_{HONO}) were acquired



simultaneously at Peking University (39.99° N, 116.31° E), which was 600 m to the west of the ICCAS site. The quantitative measurements of NO_3^- in NR-PM₁ were conducted using an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) at Beijing University of Technology (BJUT, 39.87° N, 116.48° E). The BJUT site is located between the southeastern 3rd and 4th ring roads of Beijing, representing a typical urban area similar to the ICCAS site. The NO_3^- concentration in PM_{2.5} was approximated based on the mass fraction of PM₁ in PM_{2.5}. NO_3^- accounted for 30.56 % of PM_{2.5} mass, which is consistent with the NO_3^- proportion reported in other studies during the same season in the North China Plain (Xiao et al., 2025; Xu et al., 2019). Therefore, the NO_3^- concentrations obtained in this study are reliable for further analysis.

2.2 Measurement instruments

In this study, the mixing ratios of atmospheric HONO was measured by a custom-built HONO analyzer that had been used in previous observations (Zhang et al., 2020; Tong et al., 2016; Hou et al., 2016). The measurement principle of the custom-built HONO analyzer is the same as the commercial long path absorption photometer (LOPAP) (Heland et al., 2001), and the measurement procedure is as follows. HONO is rapidly absorbed by the absorbent solution (0.06 mol L⁻¹ sulfanilamide in 1 mol L⁻¹ HCl) in a double-channel glass spiral coil, forming a stable diazonium salt which then reacts with dye solution (0.8 mmol L⁻¹ N- (1-naphthyl) ethylenediamine-dihydrochloride) to form an azo dye. The azo dye is pumped into the 50 cm liquid waveguide capillary cell (LWCC) and simultaneously detected by the spectrometer (USB2000+, Ocean Optics, USA), the optical signal is then converted into a numerical value and presented on the computer. Finally, the concentration of HONO is calculated from Lambert's law and the difference of signals between the two channels.

The relevant meteorological parameters such as temperature (T), relative humidity (RH), wind speed (WS) and wind direction (WD) were measured by the Vaisala Weather Transmitter (WXT520). The NO_x (NO and NO₂) mixing ratio was measured by a NO_x analyzer (Thermo Scientific, Model 42i) with a detection limit of 1 ppb. The mixing ratio of NH₃ was measured by an NH₃ analyzer (G2103, Picarro) using Cavity Ring-Down Spectroscopy (CRDS).

2.3 Chemical model

A zero-dimensional photochemical box model (Framework for 0-Dimensional Atmospheric Modeling–F0AM) based on RACM2 that neglects the vertical and horizontal transport processes was used to analyze the HONO budget in this study. The model was constrained by observed chemical species and meteorological parameters, with a time resolution of 1 hour. Additionally, an extra 24-hour lifetime for all species was defined in the F0AM to prevent the accumulation of secondary species to unreasonable levels. This was achieved by setting a first-order dilution rate of $1/(24 \times 60 \times 60) \text{ s}^{-1}$ and setting the background concentration of all species to zero. For more details on this part of the model, refer to Wolfe et al (Wolfe et al., 2016). The model was run from September 20 to December 23 2022, with an additional 2 days spin-up on the first day to allow intermediates to reach a steady state.



3 Results and discussion

3.1 Overview of measurement

3.1.1 General analysis of HONO and related air pollutants

Figure 1 illustrated the hourly time series of meteorological parameters and chemical species concentrations during 20 September to 23 December 2022. The specific event between 5:00–23:00 local time (LT) of December 12 was not considered in the further analysis, for the detailed reason given in Text S1 in the Supporting Information. Throughout the entire observation, there was a significant variation of temperature (Temp) and relative humidity (RH) due to span across autumn and winter. However, wind speed (WS) remained at a low level, with a range of 0.18–1.79 m s⁻¹, and the wind direction (WD) was primarily from the southeast and southwest. The meteorological conditions represented typical stagnant conditions that promoted the accumulation of pollutants in the Beijing. The HONO concentrations ranged from 0.01–4.79 ppb, with a mean value of 1.21 ± 0.94 ppb. As shown in Table 1, the highest HONO concentration in this study was generally higher than in other studies (Hou et al., 2016; Spataro et al., 2013; Li et al., 2021). This was because the stagnant conditions contributed to the accumulation of HONO (Shi et al., 2019). However, compared to previous autumn and winter in Beijing, the PM_{2.5} concentration observed in this study was significantly lower, highlighting the effectiveness of air pollution control measures implemented in recent years. General analysis of other pollutants and meteorological parameters were detailed in Text S2 of the Supporting Information.

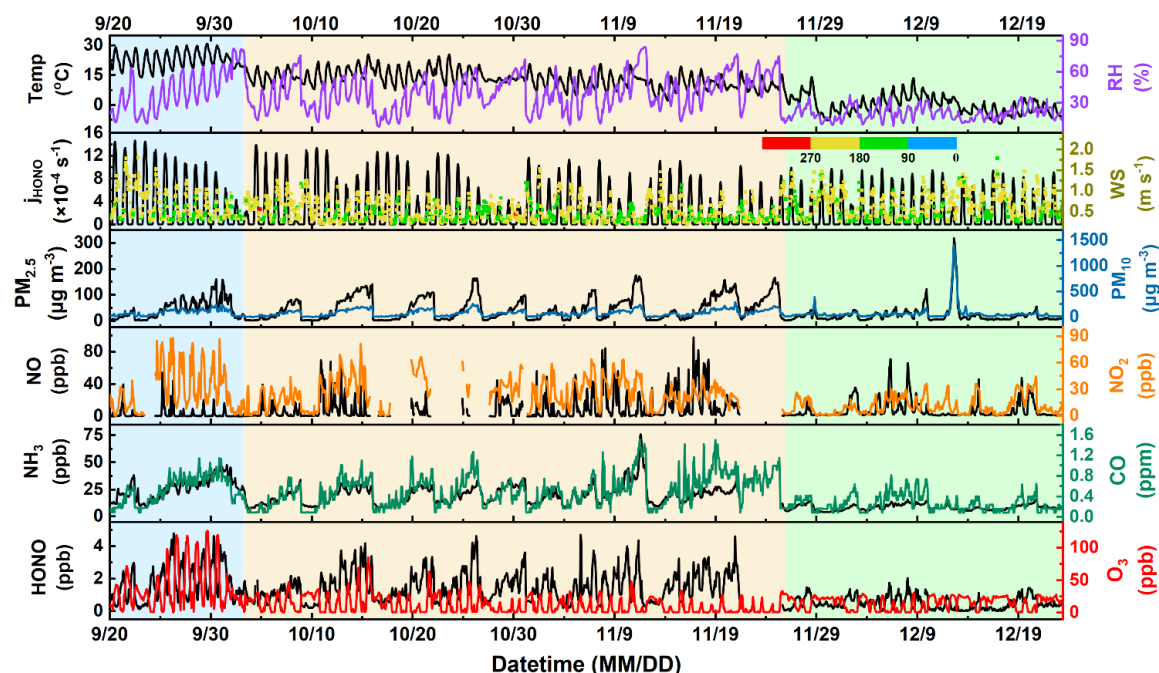


Figure 1: Hourly time series of meteorological parameters (Temp, RH, WS, j_{HONO}) and chemical species (HONO, O₃, NO, NO₂, NH₃, CO, PM_{2.5}, PM₁₀) concentrations from 20 September to 23 December 2022. The blue, yellow and green shades represent DHP, PEP and CLP, respectively.

**Table 1: Comparison of measured HONO at different sites in Beijing urban area.**

Location	Sampling periods	HONO (ppb)	HONO _{max} (ppb)	Reference
Beijing, CRAES	2019.6.13–7.4	0.44±0.24	1.39	(Li et al., 2021)
Beijing, ICCAS	2014.2.22–3.2	1.84 (Day), 2.06 (Night)	3.24	(Hou et al., 2016)
Beijing, ICCAS	2021.3.1–3.30	1.48±1.09	4.87	(Zhang et al., 2023b)
Beijing, PKU	2007.1.23–2.14	1.04±0.73	2.67	(Spataro et al., 2013)
	2007.8.2–8.31	1.45±0.58	2.91	
Beijing, BIPT	2018.8.18–9.16	0.38±0.35	1.87	(Xuan et al., 2023)
Beijing, BUCT	2017.12.1– 2018.2.28	1.38	-	(Lian et al., 2022)
Beijing, CRAES	2017.5.7–5.30	1.25±0.94	6.69	(Gu et al., 2022)
	2018.1.15–1.30	1.04±1.27	9.55	
	2018.5.25–7.15	1.27±0.44	2.41	
Beijing, IAP	2018.11.26– 2019.1.15	1.13±0.68	3.18	(Liu et al., 2021)
Beijing, ICCAS	2018.10.25–12.7	2.52±1.61	-	(Zhang et al., 2023c)
Beijing, ICCAS	2022.9.20–12.23	1.21±0.94	4.79	This work

According to the National Ambient Air Quality Standards (NAAQS), during the observation period, there were 6 days O₃ pollution when the daily maximum 8-hour average concentration of O₃ exceeded the Grade II of NAAQS (160 µg m⁻³, equivalent to 82 ppb at 25°C and 1013.25 hPa). Additionally, there were more instances of PM_{2.5} pollution days exceeding the Grade II of NAAQS (75 µg m⁻³). These days with O₃ pollution were all concentrated between September 20 and October 2, accompanying by high PM_{2.5} concentrations (up to 150 µg m⁻³). This represented a typical scenario of concurrent high levels of O₃ and PM_{2.5} pollution frequently observed in cities during autumn (Sun et al., 2009; Qu et al., 2023; Qi et al., 2024), which was associated with meteorological conditions such as relatively high solar radiation intensity, low WS and high RH (Wu et al., 2022). PM_{2.5} pollution were concentrated between October 3 and November 25. This period represented the typical periodic cycle of haze pollution observed in urban China during the autumn and winter, linked to stagnant meteorological conditions, including low air diffusion rates and high RH (Cheng et al., 2018; Zhang et al., 2014; Guo et al., 2014; Zhang et al., 2015). The concentration of PM_{2.5} exhibited a typical periodic pattern lasting 4–7 days. Each cycle began with mass concentrations below 10 µg m⁻³, which then escalated to 100 µg m⁻³ within 2–5 days, and even exceeded 150 µg m⁻³. Each PM_{2.5} pollution event consistently extended over 2–4 days, surpassing the Grade II of NAAQS (75 µg m⁻³). RH displayed a similar trend to PM_{2.5}. Additionally, the concentrations of HONO, CO, NH₃, and NO₂ progressively increased with the rise in PM_{2.5} levels, suggesting a potential connection between these gaseous pollutants and the formation of PM_{2.5},



consistent with findings from other studies conducted during the same period in autumn and winter (Slater et al., 2020; Wang et al., 2017; Zhang et al., 2023c). The period from 26 November to 23 December was marked by concentrations of gaseous pollutants (HONO, NO, NO₂, CO, NH₃, O₃) and PM_{2.5} which significantly decreased and remained at low levels, the average hourly PM_{2.5} concentration and the daily maximum 8-hour average O₃ concentration were less than the Grade I of NAAQS (35 µg m⁻³ and 100 µg m⁻³, respectively). In addition, the concentrations of HONO, NO₂, NH₃, and CO were 2–3 times lower compared to the previous two periods. Notably, the atmospheric conditions during this period were unfavorable for pollutant dispersion, characterized by low wind speeds (< 2 m s⁻¹) and predominantly southerly winds (Figure S2). However, despite these stagnant meteorological conditions, pollutant concentrations significantly decreased.

Therefore, the observation was segmented accordingly based on the concentrations of O₃ and PM_{2.5}. The period from September 20 to October 2 was characterized by double-high levels of both O₃ and PM_{2.5}, designated as Double-High Pollution Period (DHP, Blue shaded area in Figure 1). The period from October 3 to November 25 was marked by periodic cycle of PM_{2.5} pollution, identified as the PM_{2.5} Episodic-cycle Pollution Period (PEP, Yellow shaded area in Figure 1). Based on lower pollutant concentrations, the period from 26 November to 23 December was designated as the Clean Low Pollution Period (CLP, Green shaded area in Figure 1). This was markedly different from the widespread haze pollution commonly observed in Beijing during December in other studies (Zhang et al., 2019b; Tong et al., 2016), highlighting the uniqueness of this clean period.

3.1.2 Diurnal variation of chemical species across distinct pollution periods with unique characteristics

Meteorological conditions showed typical seasonal transitions from autumn to winter during the DHP, PEP and CLP, characterized by a gradual decrease in Temp and solar radiation, and a delayed sunrise time. RH exhibited an inverse diurnal pattern compared to Temp, and significantly declined during CLP. Detailed diurnal variations of meteorological parameter are provided in Text S2 and Figures S2–S3 in the Supporting Information. During the DHP, the peak PM_{2.5} concentration (60.31 µg m⁻³) appeared at 4:00 LT, then began to decrease, reaching its lowest value (29.08 µg m⁻³) at 17:00 LT, and then accumulated again at night (Figure 2). In contrast, the highest values during the PEP (52.92 µg m⁻³) and the CLP (25.58 µg m⁻³) both appeared at 20:00 LT, gradually decreasing at night and reaching their lowest values (41.06 µg m⁻³ and 12.70 µg m⁻³) at 7:00 LT. Influenced by high solar radiation intensity, intense photochemical reactions led to elevated daytime O₃ concentrations during the DHP. At the same time, higher Temp caused a large emission of volatile organic compounds (VOCs) (Qin et al., 2025; Huangfu et al., 2019; Zhang et al., 2024). The high O₃ concentrations promoted secondary organic aerosols (SOA), NO₃⁻, SO₄²⁻, and other secondary components through the gas-phase oxidation of VOCs, NO_x, and SO₂, as well as heterogeneous reactions on particle surfaces, thereby exacerbating PM_{2.5} pollution (Huang et al., 2014; Ji et al., 2024; Tao et al., 2024). Additionally, low WS and high RH under stagnant meteorological conditions further intensify the PM_{2.5} and O₃ synergistic pollution. The PEP represented typical autumn and winter haze pollution in Beijing, with characteristics similar to those reported in previous haze studies (Shen et al., 2024; Liu et al., 2023). Lower Temp and weaker sunlight reduced photochemical reactions, leading to a significant decrease in O₃ concentrations (Fu et al., 2020), which dropped to



one-third of that in the DHP. However, relatively high NO_2 concentrations and high RH promoted NO_3^- formation (Xu et al., 2019), while low WS led to more stable meteorological diffusion conditions and a lower boundary layer height (BLH), contributing to the recurrence of $\text{PM}_{2.5}$ pollution (Liu et al., 2023). During the CLP, the relatively small diurnal variation in O_3 concentrations suggested suppressed atmospheric photochemistry and a weaker oxidative capacity during this period. In addition, due to lower gaseous pollutant concentrations and lower RH, $\text{PM}_{2.5}$ concentration significantly decreased compared to the DHP and PEP. For the diurnal variations of gases pollutants, there were significant differences between three periods. During the DHP and PEP, NO , NO_2 , CO and NH_3 showed significant peaks during the morning rush hour (7:00–8:00 LT) due to vehicle emissions, then remained at lower levels throughout the daytime until concentrations began to rise again during the evening rush hour and built up during the night. In contrast, the nighttime NO concentration was also very low during the DHP, staying between 0.46–1.17 ppb, which was due to the stronger O_3 consumption of NO (Kurtenbach et al., 2012). During the CLP, the concentrations of NO , NO_2 , CO and NH_3 were lower, and their diurnal variation was not obvious. However, they still exhibited a much weaker peak around 8:00–9:00 LT, which indicated a significant reduction in vehicle emissions. The pollution characteristics of the three periods exhibited both distinct differences and certain similarities, forming a sharp vertical contrast while also allowing for horizontal comparisons with results from the same periods in other studies.

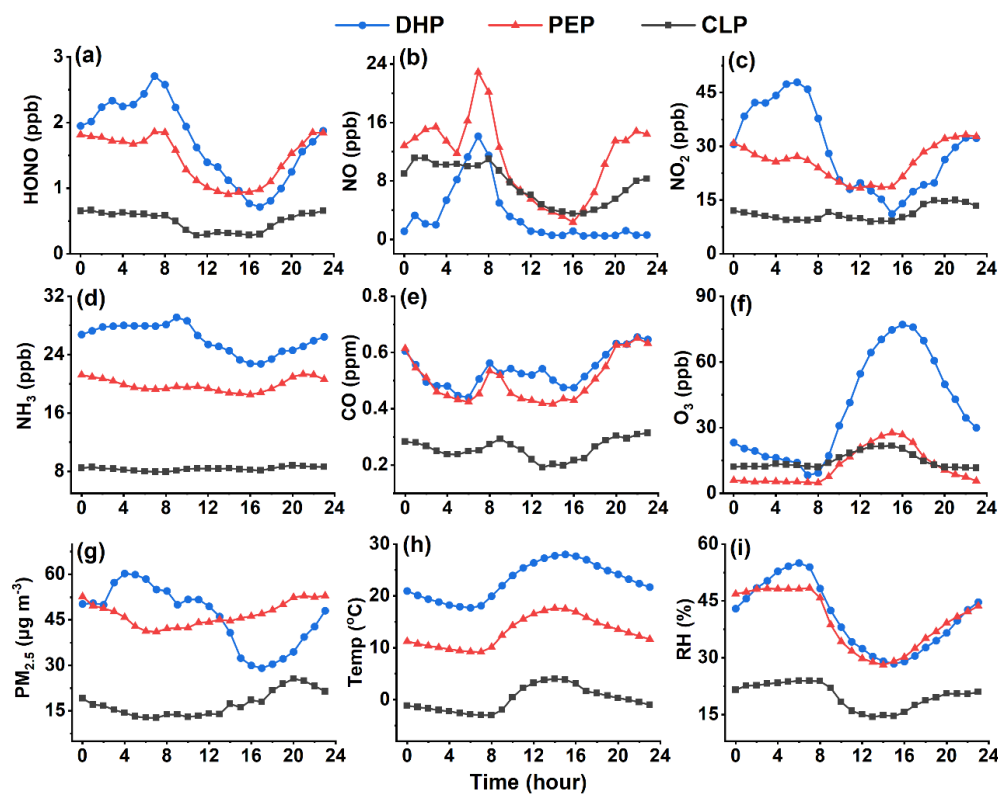


Figure 2: The diurnal variations of chemical species (HONO , NO , NO_2 , NH_3 , CO , O_3 , $\text{PM}_{2.5}$) and meteorological parameters (Temp, RH) during three periods. The blue, red, and black dotted line graphs represent DHP, PEP and CLP, respectively.



HONO and NO_x (the main precursors of HONO) exhibited similar diurnal variation trends, with higher at night and lower during the day. Specifically, during the DHP and PEP, HONO concentrations significantly peaked at 7:00–8:00 LT (2.71 ppb and 1.86 ppb, respectively) due to nocturnal formation and accumulation as well as direct vehicles emissions in the morning rush hour, then declined due to rapid photolysis in the daytime. Subsequently, due to the absence of photolysis reactions and the arrival of the evening rush hour, HONO concentration began to accumulate, remaining at a high level throughout the night (1.94–2.33 ppb and 1.67–1.81 ppb, respectively). This phenomenon was also observed in previous studies during PM_{2.5} and O₃ pollution in autumn and winter in Beijing (Jia et al., 2020; Li et al., 2021; Liu et al., 2021), which indicated that HONO was a crucial precursor in driving the formation of PM_{2.5} and O₃ pollution. Due to the difference in sunrise time and photolysis processes, the peak HONO concentration during the PEP occurred 1 hour later in the morning compared to the DHP. Wang et al. also observed that the decline in HONO concentration varied seasonally with sunrise times, being around 8:00 LT in winter, around 7:00 LT in autumn, and around 6:00 LT in summer and spring (Wang et al., 2017). During the CLP, HONO concentration significantly decreased and remained at low level (0.28–0.66 ppb). Due to nighttime formation and accumulation, HONO concentration peaked (0.66 ppb) around midnight, then slowly decreased before sunrise. HONO concentration did not show a significant increase during the morning rush hour (7:00–8:00 LT), indicating a substantial reduction in vehicle emissions during the CLP. HONO concentration decreased to its minimum value (0.28 ppb) at 11:00 LT, then showed an increase around noon, reaching 0.33 ppb at 13:00 LT. Subsequently, HONO began to accumulate again as the sunlight intensity weakened, maintaining levels between 0.55–0.66 ppb throughout the night.

In summary, the DHP and PEP represented common pollution scenarios during the autumn and winter in Beijing, with HONO concentration levels and diurnal variation comparable to those reported in previous studies (Liu et al., 2021; Zhang et al., 2023a; Slater et al., 2020). However, the CLP observed in this study, which occurred during the frequent winter haze pollution period (November 26 to December 23), differed significantly from the pollution situation in Beijing urban area during the same period in other studies. For example, Tong et al. observed PM_{2.5} pollution events (with average PM_{2.5} concentrations up to 144 $\mu\text{g m}^{-3}$) accompanied by high HONO concentrations (3 ppb) in urban Beijing from 12 to 22 December 2015 (Tong et al., 2016). Zhang et al. captured a severe haze period with PM_{2.5} concentrations reaching 418 $\mu\text{g m}^{-3}$ and HONO concentrations reaching 5.8 ppb at the same site from 16 to 24 December 2016, while a clean period brought by strong winds was also observed (Zhang et al., 2019b). Liu et al. also observed haze pollution in urban Beijing in December 2018 (Liu et al., 2021). Further analysis revealed that the Traffic Performance Index (TPI) in Beijing was relatively low at 3.01 in December 2022, significantly lower than usual, indicating reduced vehicle emissions accompanied by a significant decrease in anthropogenic activities. Compared to September, October, and November 2022, the TPI decreased by 53 %, 41 %, and 25 %, respectively. Compared to December 2021, the decrease was as high as 55 % (<https://www.bjtrc.org.cn/List/index/cid/7.html>). These findings demonstrated that even under stagnant regional meteorological conditions, a substantial reduction in direct anthropogenic activities could lead to significant air quality improvements, resulting in cleaner period. Considering the rapid urbanization in China and the sharp increase in vehicle ownership, these findings may also be applicable to other cities or highly industrialized regions, offering valuable insights



for formulating scientifically effective emission reduction policies. The following sections will further explore the source contributions of HONO under different pollution scenarios and quantify the specific impact of direct emission reductions on improving PM_{2.5} and O₃ pollution.

250 3.2 HONO budget during nighttime

Vehicle emissions are the most important direct source of HONO in urban areas (Xu et al., 2015; Yun et al., 2017; Yin et al., 2023). As described in diurnal variations and previous studies, CO and NO were major pollutants originating from combustion processes and could be directly emitted into the atmosphere through vehicle emissions in urban areas (Sun et al., 2014; Bond et al., 2013). HONO exhibited a positive correlation with NO or CO, indicating that vehicle emissions played an important role in HONO formation at this observation site (Figure S4). However, it is noteworthy that during the DHP and PEP, which had higher TPI values, the correlation between HONO and NO or CO was lower than that in the CLP. The higher intensity of anthropogenic activities in these periods led to a significant increase in PM_{2.5} and NO₂ concentrations, which in turn enhanced the secondary formation of nighttime HONO (e.g., NO₂ heterogeneous reaction on various surfaces), making it the dominant process. In contrast, the lower PM_{2.5} concentrations weaken the contribution of secondary HONO formation during the CLP, resulting in a more pronounced correlation between vehicle emissions and nighttime HONO formation (Jia et al., 2020). To assess the impact of vehicle emissions in this observation, the local emission factor EF_{emis} (=ΔHONO/ΔNO_x) was derived based on ambient measurements. As described in Text S3 and Table S2 in the Supporting Information, the minimum EF_{emis} (0.0051) in fresh plumes was taken as the upper limit for the direct emission factor to minimize the influence of secondary HONO formation (Su et al., 2008), which was comparable to the value of 0.0051 measured in Beijing (Zhang et al., 2022b), 0.0053 measured in Ji'nan (Li et al., 2018a) and 0.005 measured in Hong Kong (Xu et al., 2015). Since the types of vehicles around this site had not changed, it was reasonable to use the same EF_{emis} (0.0051) to assess the contribution of vehicle emission to the HONO through the entire observation period. As shown in Figure 3(a), the levels of directly emitted HONO (HONO_{emis}) were comparable during the DHP and PEP, while significantly lower during the CLP. HONO_{emis} exhibited significant increases in the evening (~19:00 LT) and early morning (~6:00 LT) during the DHP and PEP, likely associated with enhanced vehicle emissions during the morning and evening rush hours. In contrast, no significant increases in HONO_{emis} were observed during the CLP, and its nighttime variation remained weak. Although HONO_{emis} were relatively high during the DHP and PEP (Figure 3(a)), the contribution of direct emissions was lower than that in the CLP, due to the greater influence of other sources. Vehicle emissions accounted for 9.6 %, 11.7 %, and 17.6 % of nighttime HONO during the DHP, PEP, and CLP, respectively, indicating that the relative importance of direct emissions increases under cleaner period, which was consistent with previous studies (Jia et al., 2020; Zhang et al., 2022b).

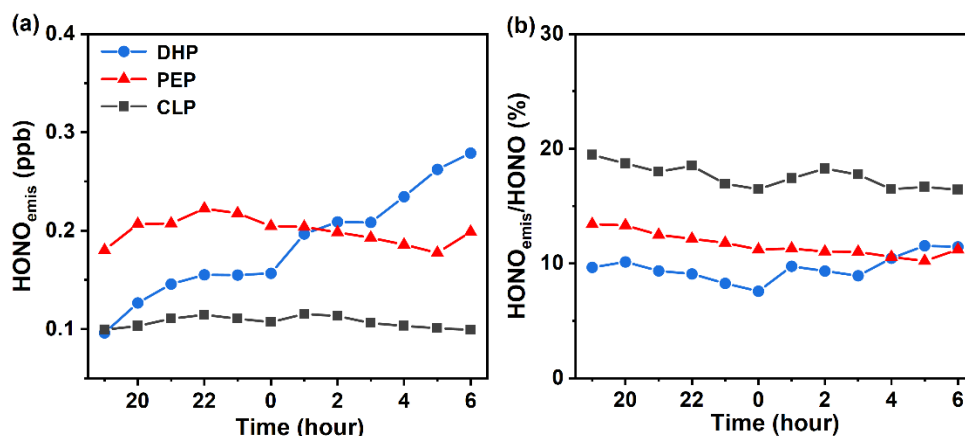


Figure 3: The hourly variations of (a) HONO_{emis} and (b) HONO_{emis}/HONO at nighttime during three periods. The blue, red, and black dotted line graphs represent DHP, PEP and CLP, respectively.

The heterogeneous reactions of NO₂ on various surfaces were widely recognized as the primary secondary source of HONO (Spataro and Ianniello, 2014; Kebede et al., 2016; Indarto, 2011). To mitigate the influence of direct emissions, HONO_{corr} (HONO-HONO_{emis}) was utilized for further analysis. The HONO_{corr}/NO₂ ratio was often used to represent the heterogeneous conversion fraction of NO₂ to HONO due to its first-order dependence on NO₂ (Li et al., 2012; Jenkin et al., 1988). The HONO_{corr}/NO₂ ratio in DHP, PEP, and CLP were 0.101, 0.076, and 0.076, respectively, which were higher than previous studies (Zhang et al., 2023c; Zhang et al., 2022a; Cui et al., 2018). This indicated that the potential for heterogeneous conversion from NO₂ to HONO was stronger during this observation, especially in DHP. The dominant medium for the heterogeneous conversion of NO₂ has been a contentious issue whether aerosol surfaces or ground surfaces are more important. Due to the absence of measurements of aerosol surface density (SA) in this observation, PM_{2.5} concentrations were used as a substitute to determine the impact of aerosols on the conversion of NO₂ to HONO at nighttime (Lu et al., 2018; Cai et al., 2017). The relationship of HONO_{corr} with NO₂ and NO₂×PM_{2.5} was demonstrated in Figure S6. HONO_{corr} exhibited a significant positive correlation with NO₂, with correlation coefficients (R²) of 0.66, 0.45, and 0.38 during the DHP, PEP, and CLP, respectively, indicating that the heterogeneous reaction of NO₂ was an important source of HONO in this observation. Additionally, the R² between HONO_{corr} and NO₂×PM_{2.5} was 0.72, 0.48, and 0.35 for the three periods, suggesting that the heterogeneous reaction of NO₂ on aerosol contributed to HONO formation during the DHP and PEP, which was closely associated with the higher PM_{2.5} concentrations providing more reactive surfaces. However, compared to previous studies conducted in Beijing during autumn and winter, the correlation between HONO_{corr} and NO₂×PM_{2.5} during the DHP and PEP was significantly lower (Tong et al., 2015; Nie et al., 2015). For example, Yan et al. (Yan et al., 2015) and Zhang et al. (Zhang et al., 2019b) reported that during haze pollution events in Beijing in the mid-2010s, the average PM_{2.5} concentration could reach approximately 130 μg m⁻³, with levels during severe haze episodes approaching 311 μg m⁻³. In contrast, the average PM_{2.5} concentration during the DHP and PEP in this study was only around 46 μg m⁻³. This discrepancy may be attributed to the implementation of air pollution control policies in recent years, which led to a substantial reduction



in PM_{2.5} concentrations in Beijing compared to previous years (Huang et al., 2021; Guha et al., 2024), thereby limiting the heterogeneous reactions of NO₂ on aerosols. Particularly during the CLP, PM_{2.5} concentrations decreased by 63 % compared to the DHP and PEP, further weakening the role of aerosol in NO₂ heterogeneous reactions to produce HONO. Consequently, compared to NO₂ heterogeneous reactions on ground surfaces, its reaction on aerosol played a more limited role in HONO formation. Notably, HONO_{corr} exhibited the strongest correlation with both NO₂ and NO₂×PM_{2.5} during the DHP, likely due to enhanced oxidation of organic and inorganic components, altering the surface reactivity and consequently promoting NO₂ conversion to HONO (George et al., 2015; Ndour et al., 2008).

It was observed that the HONO_{corr}/NO₂ ratios increased with the increase in RH (<70 %), indicating that the absorbed water on the surface participated in the heterogeneous reactions of NO₂ to HONO (Stutz et al., 2004). Furthermore, once RH exceeded a critical threshold (≥70 %) (Dark blue dots in the Figure S6 (a–b)), the heterogeneous reactions of NO₂ on various surfaces were inhibited, leading to a decrease in HONO_{corr}/NO₂ with increasing RH. Similar segmented correlations between HONO_{corr} and RH had been observed in previous studies, which had been interpreted as evidence of the nonlinear dependence of NO₂ to HONO conversion efficiency on RH (Qin et al., 2009; Li et al., 2012; Tong et al., 2015). One possible explanation was that the quantity of water layers formed on various surfaces rapidly increased with rising RH, resulting in effective uptake of HONO and making the surfaces less accessible or reducing their reactivity with NO₂ (Yu et al., 2022; Li et al., 2021).

3.3 Model simulations for HONO sources and sinks

The base sources of HONO in the model simulation only included the homogeneous reaction of NO with OH (S_{NO+OH}), while the sinks of HONO included the dry deposition of HONO (L_{dep}), the photolysis of HONO (L_{photo}), and the homogeneous reaction of HONO with OH (L_{HONO+OH}). The base model could only explain 3.5 %, 18.4 %, and 18.3 % of the observed HONO (HONO_{obs}) during the DHP, PEP, and CLP, respectively, further lead to an underestimation of OH and O₃ concentrations in the atmosphere (Liu et al., 2019b; Tie et al., 2019). The proportion of soil near the site was minimal and primarily used for landscaping, with almost no fertilization activities. Moreover, the NH₃ concentration was significantly lower than that observed in rural areas of North China where soil emissions were considered (Xue et al., 2021). Therefore, soil emissions were not included in the model. Other known sources of HONO were incorporated into the model simulations, including vehicle direct emissions (S_{eims}), the heterogeneous reactions of NO₂ on ground surfaces (S_{NO₂-g}) and aerosol surfaces (S_{NO₂-a}), the photo-enhanced heterogeneous reactions of NO₂ on ground surfaces (S_{NO₂-g, hv}) and aerosol surfaces (S_{NO₂-a, hv}), as well as the photolysis of nitrate (S_{NO₃, hv}). The parameterization mechanisms for the production and removal pathways of HONO were detailed in Table 2, and the specific parameter values were presented in Text S5 of the Supporting Information.

Table 2: Parameterized HONO production/loss mechanisms in model simulations.



Source/ Loss	RACM Mechanisms	Parametrization
S_{emis}	Direct emission	$EF_{emis}=0.0051$
S_{NO+OH}	$NO + OH \rightarrow HONO$	k_{OH+NO}
$S_{NO_2_g}$	$2NO_2 + H_2O \xrightarrow{\text{ground surface}} HONO + HNO_3$	$k_{het-g} = \frac{1}{8} \times v_{NO_2} \times \frac{1}{MLH} \times \gamma_g$
$S_{NO_2_a}$	$2NO_2 + H_2O \xrightarrow{\text{aerosol surface}} HONO + HNO_3$	$k_{het-a} = \frac{1}{8} \times v_{NO_2} \times SA \times \gamma_a$
$S_{NO_2_g, hv}$	$2NO_2 + H_2O + hv \xrightarrow{\text{ground surface}} HONO + HNO_3$	$k_{het-g, hv} = \frac{1}{4} \times v_{NO_2} \times \frac{1}{MLH} \times \gamma_{g, hv} \times \frac{j_{NO_2}}{0.005 s^{-1}}$
$S_{NO_2_a, hv}$	$2NO_2 + H_2O + hv \xrightarrow{\text{aerosol surface}} HONO + HNO_3$	$k_{het-a, hv} = \frac{1}{4} \times v_{NO_2} \times SA \times \gamma_{a, hv} \times \frac{j_{NO_2}}{0.005 s^{-1}}$
$S_{NO_3^-, hv}$	$NO_3^- + hv \rightarrow 0.67HONO + 0.33NO_x$	$k_{NO_3^-, hv} = EF \times j_{HNO_3}$
L_{photo}	$HONO + hv \rightarrow OH + NO$	j_{HONO}
$L_{HONO+OH}$	$HONO + OH \rightarrow NO_2 + H_2O$	$k_{OH+HONO}$
L_{dep}	HONO deposition	$k = \frac{V_{HONO}}{BLH}$

After incorporating all HONO sources listed in Table 2, the diurnal variation of simulated HONO ($HONO_{sim,0}$) from different sources was illustrated in Figure 4. The heterogeneous reaction of NO_2 on ground (including $S_{NO_2_g}$ and $S_{NO_2_g, hv}$) was the main source of HONO during the observations, contributing 44.6 %, 37.6 %, and 44.2 % to $HONO_{sim,0}$ in DHP, PEP, and CLP, respectively. The heterogeneous reaction of NO_2 on aerosol surfaces (including $S_{NO_2_a}$ and $S_{NO_2_a, hv}$) contributed 16.2 %, 14.6 %, and 10.4 % to $HONO_{sim,0}$ reflecting the variation in $PM_{2.5}$ concentrations across the three periods (Table S1). The heterogeneous reactions of NO_2 (on ground and aerosol surfaces) contributed over 50 % of $HONO_{sim,0}$, comparable to previous research, 54.4 % in the Yangtze River Delta region (Shi et al., 2020), and 63 % in urban areas of Beijing (Zhang et al., 2023b). NO_3^- photolysis contributed 12.6 %, 11.8 %, and 4.8 % to $HONO_{sim,0}$ during the DHP, PEP, and CLP, respectively. Although traditionally considered minor (Xue et al., 2020; Zhang et al., 2022b), our results suggested that its importance increases under more polluted conditions due to elevated particulate nitrate levels (Zhai et al., 2021; Xu et al., 2019; Xiao et al., 2025). While still lower than the 31–36 % reported in southern China (Fu et al., 2019), NO_3^- photolysis remained a non-negligible source. The homogeneous reaction of NO with OH radicals typically peaked around 8:00–9:00 LT, contributing 8.3 %, 22.6 %, and 20.0 % during the three periods. Vehicle emissions accounted for 18.3 %, 13.4 %, and 20.6 %, with a relatively higher contribution during cleaner periods, consistent with previous studies (Jia et al., 2020). Despite including all known sources, a notable portion of $HONO_{obs}$ remained unexplained. The unknown HONO



concentration ($\text{HONO}_{\text{unknown}} = \text{HONO}_{\text{obs}} - \text{HONO}_{\text{sim},0}$) accounted for 51.8%, 16.6%, and 6.8% during the three periods, respectively. Notably, the $\text{HONO}_{\text{unknown}}/\text{HONO}_{\text{obs}}$ increased with pollution severity (higher $\text{PM}_{2.5}$ and O_3), suggesting the existence of additional unidentified sources or processes under complex pollution conditions. Overall, while the model captures the major known sources of HONO, the high proportion of unexplained HONO during heavily polluted periods highlights the need for further investigation into missing mechanisms.

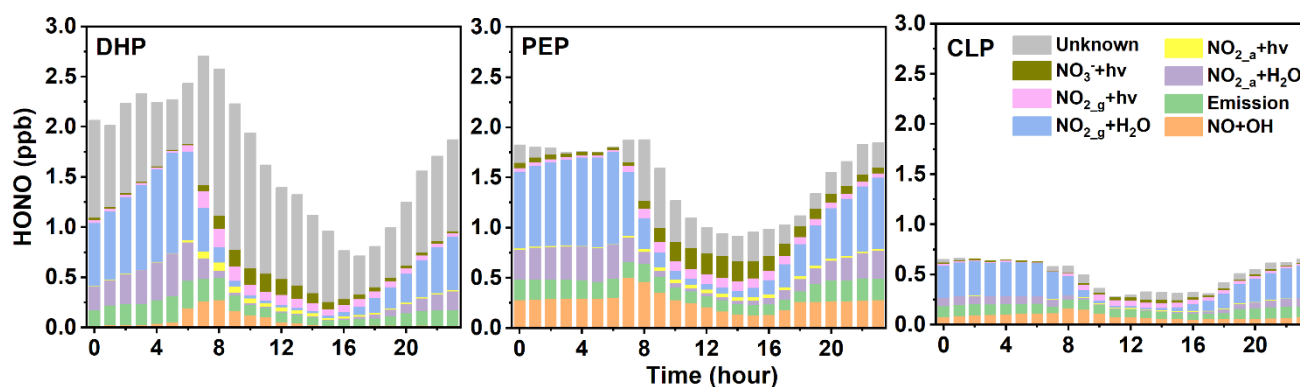


Figure 4: The diurnal variations of the $\text{HONO}_{\text{sim},0}$ from different sources during the DHP, PEP and CLP.

To further investigate the formation mechanisms of $\text{HONO}_{\text{unknown}}$, this study employed a time-segmented analysis approach. The transitional periods between day and night (i.e., three hours before and after sunrise and sunset) were excluded, then separately analyzing representative daytime (10:00–15:00 LT) and nighttime (22:00–03:00 LT) episodes. This time-segmented analysis approach effectively avoided the interference of diurnal transitions, allowing for a clearer distinction of the characteristics of $\text{HONO}_{\text{unknown}}$ during different episodes. Due to the rapid photolysis of HONO around noontime, the production rate of $\text{HONO}_{\text{unknown}}$ (P_{unknown}) during the daytime could be expressed by the following equation:

$$P_{\text{unknown}} = \text{HONO}_{\text{unknown}} \times j_{\text{HONO}}$$

P_{unknown} exhibited a positive correlation with $\text{OH} \times j_{\text{HONO}}$, with R^2 of 0.69 (Figure S8), suggesting that daytime $\text{HONO}_{\text{unknown}}$ might act as a sink for OH radicals. This result was consistent with our previous studies conducted through ground (Lin et al., 2022; Zhang et al., 2023b) and vertical observations (Zhang et al., 2020) in urban Beijing. Through linear regression analysis of nighttime $\text{HONO}_{\text{unknown}}$ with other pollutants and meteorological parameters, significant positive correlations between $\text{HONO}_{\text{unknown}}$ and RH, NO_2 , $\text{PM}_{2.5}$, NH_3 , and CO were observed (Figure S9). Given the strong correlations between CO and $\text{PM}_{2.5}$ ($R^2=0.54$) and NH_3 ($R^2=0.59$), these pollutants were likely to share common sources, which could explain the observed good correlation between CO and $\text{HONO}_{\text{unknown}}$. Further multivariate linear regression analysis revealed that, compared to individual pollutants, the composite parameter $\text{NO}_2 \times \text{NH}_3 \times \text{RH}$ exhibited a significantly stronger correlation with $\text{HONO}_{\text{unknown}}$. This finding suggested that $\text{HONO}_{\text{unknown}}$ may be related to NH_3 -promoted heterogeneous reactions of NO_2 , with RH playing a crucial role in this process. Li et al. proposed that NH_3 could promote the hydrolysis of NO_2 at the air-water interface to produce HONO, which could be an important pathway for HONO production in NH_3 -rich environments (Li et al., 2018b). Additionally, our group's previous research on haze pollution during the autumn and winter of 2018



demonstrated that the synergistic effect of RH and NH₃ significantly enhanced the NO₂ heterogeneous conversion to HONO, leading to a positive feedback mechanism between haze pollution and HONO production (Zhang et al., 2023c). Notably, RH and NO₂ levels at nighttime in the DHP and PEP were comparable to those observed during haze pollution episodes in the autumn and winter of 2018. Therefore, the enhancement factor ($f_{\text{NH}_3, \text{RH}}$) from Zhang et al.'s work for nighttime HONO production in the model simulation was applied. Since RH remained consistently below 40 % during the CLP, $f_{\text{NH}_3, \text{RH}}$ was set to 1. Additionally, an extra HONO source, enhanced by photolysis and consuming OH radicals, was introduced for daytime HONO production during three periods. The revised simulation results (HONO_{sim,1}) showed good agreement with HONO_{obs}, successfully reproducing the HONO variations during three periods (Figure 5). Due to intermittent light rain, the model exhibited slightly reduced performance during certain periods, such as on September 22 and October 3. These findings have important implications for future studies. First, pathways related to solar radiation and OH radicals should be considered in future studies on daytime HONO sources. Second, for typical pollution events characterized by high relative humidity (RH > 40 %) and elevated NH₃ concentrations (> 10 ppb), the synergistic effect of RH and NH₃ in promoting NO₂ heterogeneous reactions at the air-water interface should be fully considered. These insights provide a critical basis for improving parameterization schemes of HONO formation mechanisms in atmospheric chemistry models.

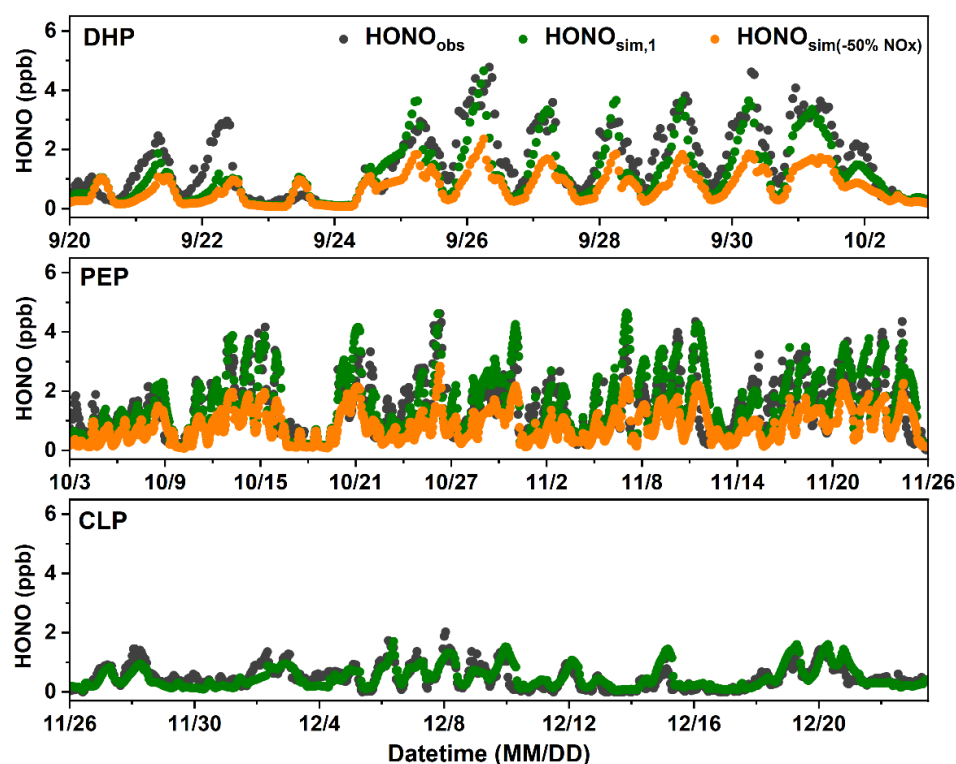


Figure 5: Time series of observed HONO and simulated HONO under different scenarios during the DHP, PEP, and CLP. The black scatter points represent observed HONO (HONO_{obs}), the green scatter points represent the revised simulated HONO (HONO_{sim,1}), the orange scatter points represent simulated HONO after a 50 % reduction in NO_x emissions (HONO_{sim(-50% NO_x)}). The data had a temporal resolution of 1 hour.



As mentioned in the "Overview of measurement", the TPI in December decreased by approximately 50 % compared to September and October, reflecting a significant reduction in anthropogenic activities. To directly assess the impact of reduced anthropogenic activities on atmospheric HONO, we assumed a 50 % reduction in NO_x emissions during the DHP and PEP due to decreased anthropogenic activities. This NO_x reduction scenario was incorporated as a constraint in the model to obtain simulated HONO concentrations (HONO_{sim(-50 % NO_x)}). The simulation results (orange scatter points in Figure 5) indicated that NO_x reduction led to significant reductions in HONO levels, with declined of 33.7 % and 38.4 % during the DHP and PEP, respectively. These quantitative results confirmed that reduced anthropogenic activities could effectively suppress atmospheric HONO formation, thereby positively contributing to improved air quality. In summary, this study provided the first direct evidence through scenario simulations that reducing anthropogenic activities was a key strategy for controlling atmospheric HONO levels in autumn and winter in Beijing, thereby limiting the formation of secondary pollutants such as PM_{2.5} and O₃. These findings offered important scientific support for formulating effective pollution control strategies.

4 Conclusions

Here, we presented measurements of HONO in urban Beijing during the autumn and winter of 2022, combined with a box model based on RACM2 to analyze its variation patterns and source mechanisms under three typical pollution periods. Particular attention was given to unidentified HONO sources and their implications for atmospheric chemistry. Our study identified three distinct pollution scenarios: Double-High Pollution period of O₃ and PM_{2.5} (DHP), PM_{2.5} Episodic-cycle Pollution period (PEP), and Clean Low Pollution period (CLP). Notably, stagnant meteorological conditions predominated, characterized by low wind speeds and southerly winds, suggesting that variations in pollutant concentrations were mainly driven by local emissions associated with anthropogenic activities. The HONO variation characteristics exhibited similarities and differences across three periods. The average HONO concentrations were 1.71 ppb and 1.46 ppb during the DHP and PEP, respectively, while it decreased more than threefold to 0.50 ppb during the CLP. HONO exhibited similar diurnal variation trends in three periods, with higher at night and lower during the day. Other pollutants (NO₂, NH₃, CO, and PM_{2.5}) also showed significantly lower levels (2–3 times) during the CLP compared to the DHP and PEP, while NO concentrations were lowest during the DHP. O₃ concentration was highest during the DHP and were similar during the PEP and CLP. The differences in pollutant concentration were related to the distinct HONO formation mechanisms and conversion frequencies during three periods, reflecting the variations in atmospheric chemical processes. The contribution of vehicle emission to nighttime HONO was highest during the CLP. During the DHP and PEP, stronger correlations between nighttime HONO with PM_{2.5} and NO₂ indicated a greater contribution from heterogeneous reactions, thereby reducing the relative impact of vehicle emission. The NO₂ heterogeneous reaction on ground was dominant HONO source in all periods, contributing 44.6 %, 37.6 %, and 44.2 % of simulated HONO, respectively. NO₂ heterogeneous reactions on aerosol surfaces contributed 16.2 %, 14.6 %, and 10.6 % in all periods, respectively. NO₃⁻ photolysis accounted



for 12.6 %, 11.8 %, and 4.8 %, consistent with $PM_{2.5}$ concentrations in three periods, and indicating increasing NO_3^- fractions in $PM_{2.5}$ under more polluted conditions. The homogeneous reaction of NO with OH contributed 8.3 %, 22.6 %, and 20.0 %, respectively. Notably, although overall anthropogenic emissions were lower during the CLP, the relative contribution of vehicle emissions to HONO became more significant. Despite incorporating all known sources into the model, significant missing HONO sources remained during three periods, accounting for 51.8 %, 16.6 %, and 6.8 %, respectively. Correlation analysis indicated that daytime $HONO_{unknown}$ was associated with solar radiation and OH radical consumption, while nighttime $HONO_{unknown}$ was related to NH_3 -promoted heterogeneous reactions of NO_2 . Including these pathways in the model significantly reproduced observed HONO. Based on TPI and scenario simulations, a 50 % reduction in NO_x emissions due to decreased anthropogenic activities during the DHP and PEP would lead to a 33.7 % and 38.4 % decrease in HONO concentrations, respectively.

In summary, based on comprehensive observations and model simulations of HONO in Beijing during the autumn and winter, this study elucidated the primary source characteristics of HONO under different typical pollution periods and quantitatively assessed the direct impact of anthropogenic activities variation on its formation. The results highlighted the critical role of controlling anthropogenic emissions in improving air quality and provide strong scientific support for formulating effective air pollution control strategies in urban areas. However, this study focused on urban environments during the autumn and winter, and a systematic understanding of how anthropogenic activities variation influence HONO in suburban and rural regions remains lacking. Future research should integrate multi-site and multi-seasonal observations with laboratory studies and regional chemical transport modeling to improve our understanding of HONO sources and atmospheric chemistry, and to quantitatively evaluate the impact of anthropogenic activities variation on air quality across different environments.

Data availability

The data presented in this study can be accessed through <https://doi.org/10.5281/zenodo.16083849> (Zhai et al., 2025)

Supplement

The supplement will be published alongside this article.

Author contribution

ZMZ contributed to methodology, data curation and analysis, and original draft writing. TSR contributed to conceptualization, investigation, data curation, writing, review and editing, supervision, and funding acquisition. ZWQ and ZHL contributed to data analysis, result discussion, and manuscript commenting. LX and WXQ participated in observational



studies and data curation. GMF contributed to conceptualization, investigation, manuscript review, supervision, and funding acquisition.

Competing interests

455 The contact author has declared that none of the authors has any competing interests.

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