Budget of nitrous acid (HONO) at an urban site in the fall season of Guangzhou, China

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Abstract. High concentrations of nitrous acid (HONO) have been observed in the Pearl River Delta (PRD) region of China in recent years, contributing to elevated atmospheric oxidation capacity by producing OH through HONO photolysis. We have investigated budget of HONO at an urban site in Guangzhou from 27 September to 9 November 2018 using data from a comprehensive atmospheric observation campaign. During this period, HONO was measured from 0.02 to 4.43 ppbv with an average of 0.74 ± 0.70 ppbv. Emission ratios (HONO/NOx) of $0.9 \pm 0.4\%$ were derived from 11 fresh plumes. The primary emission rate of HONO at night was calculated to be between 0.04 ± 0.02 ppbv h^{-1} and 0.30 ± 0.15 ppbv h^{-1} based on a high-resolution NOx emission inventory. Heterogeneous conversion of NO_2 on ground surface (0.27 ± 0.13 ppbv h^{-1}), primary emission from vehicle exhaust (between 0.04 ± 0.02 ppbv h^{-1} and 0.30 ± 0.15 ppbv h^{-1} with a middle value of 0.16 ± 0.07 ppbv h^{-1}) and the homogeneous reaction of NO + OH (0.14 ± 0.30 ppbv h^{-1}) were found to be the three largest sources of HONO at night. Heterogeneous NO_2 conversion on the aerosol surfaces (0.03 ± 0.02 ppbv h^{-1}) and soil emission (0.019 ± 0.009 ppbv h^{-1}) were two other minor sources. Correlation analysis shows that NH_3 and relative humidity (RH) may have participated in the heterogeneous transformation from NO_2 to HONO at night. Dry deposition (0.41 ± 0.31 ppbv h^{-1}) was the largest removal process of HONO at night, followed by dilution (0.18 ± 0.16 ppbv h^{-1}), while HONO loss on aerosol surfaces was much slower (0.008 ± 0.006 ppbv h^{-1}). In the daytime, the average primary emission P_{emis} was 0.12 ± 0.02 ppbv h^{-1}, and the homogeneous reaction P_{OH+NO} was 0.79 ± 0.61 ppbv h^{-1}, larger than the unknown source $P_{Unknown}$ (0.65 ± 0.46 ppbv h^{-1}). Similar to previous studies, $P_{Unknown}$ appeared to be related to the photo-enhanced conversion of NO_2.

Our results show that primary emissions and reaction of NO + OH can significantly affect HONO at a site with intensive emissions, both during daytime and nighttime. The impact of uncertain parameter values assumed in the calculation of HONO sources can have strong impact on the relative importance of HONO sources at night, and could be reduced by

35   improving knowledge on key parameters such as the NO_2 uptake coefficient. The uncertainty with estimating direct emission can be reduced by using emission data with higher resolution and quality. Our study highlights the importance of better constraining both conventional and novel HONO sources by reducing uncertainties in their key parameters in advancing our knowledge on this important source of atmospheric OH.

40   Keywords: HONO; Budget analysis; Heterogeneous reaction; Uncertainty

1 Introduction

Nitrous acid (HONO) is an important primary source of hydroxyl radical (OH) through photolysis (Reaction R1), contributing up to 33–92% OH at rural and urban sites (Kleffmann et al., 2005; Michoud et al., 2012; Tan et al., 2017; Xue et al., 2020; Hendrick et al., 2014). OH is the principle atmospheric oxidant that is responsible for oxidizing and removing

45   most natural and anthropogenic trace gases. OH initiates the oxidation of the volatile organic compounds (VOC) to produce hydroperoxyl radicals (HO_2) and organic peroxy radicals (RO_2), which further lead to the formation of ground-level ozone (O_3) in the presence of nitrogen oxides ($NOx = NO + NO_2$) (Xue et al., 2016; Finlayson-Pitts and Pitts, 2000; Hofzumahaus et al., 2009; Lelieveld et al., 2016; Tan et al., 2018), as well as secondary organic aerosols (SOA). However, the detailed formation mechanisms of HONO are still not well understood and the observed HONO concentrations cannot be completely

50   explained by current knowledge (Sörgel et al., 2011a; Kleffmann et al., 2005; Liu et al., 2019a; Lee et al., 2016; Liu et al., 2020b; Pusede et al., 2015).

$$HONO + hv \rightarrow OH + NO \ (300 \ nm < \lambda < 405 \ nm) \tag{R1}$$

55   So far numerous HONO sources have been found, and they can be categoried as direct emissions, homogeneous reactions and heterogeneous reactions. Fossil fuel combustion is the most important direct emission source of HONO (Kurtenbach et al., 2001; Kirchstetter et al., 1996; Rappenglück et al., 2013; Kramer et al., 2020; Xu et al., 2015; Trinh et al., 2017). In general, the emission ratios of HONO/NOx obtained from fresh air masses mixed with vehicle exhaust (0.03%–1.7%) (Kurtenbach et al., 2001; Kirchstetter et al., 1996; Rappenglück et al., 2013; Trinh et al., 2017; Liu et al., 2017; Pitts et al.,

60   1984; Nakashima and Kajii, 2017) are much smaller than the ratios of HONO/NOx observed in the low boundery layer (2.3%–9%) (Yang et al., 2014; Zhou et al., 2002a; Hao et al., 2020; Gu et al., 2021; Li et al., 2018a; Yu et al., 2009; Acker et al., 2006; Kleffmann et al., 2003; VandenBoer et al., 2013; Vogel et al., 2003), reflecting substantial secondary formation of HONO away from direct emissions. Recent studies found that soil emission might be another major direct emission source of HONO (Su et al., 2011; Oswald et al., 2013; Weber et al., 2015; Wu et al., 2019; Wang et al., 2021b), although the

65   confirmation of its atmospheric significance requires further comparisons between laboratory and field measurements. It

should be noted that direct emissions may surpass secondary sources at sampling sites with heavy emission impacts (Liu et al., 2019a; Tong et al., 2015; Zhang et al., 2019; Tong et al., 2016; Meusel et al., 2016).

70 Homogeneous gas-phase reaction between NO and OH (R2) is the most well known secondary source of HONO (Perner and Platt, 1979). HONO concentrations measured in the atmosphere cannot be explained by direct emission and this reaction alone, especially during daytime (Kleffmann et al., 2005; Lee et al., 2016) when a large source of HONO is necessary to sustain the measured level of HONO against fast photolysis. Some homogeneous HONO formation mechanisms have been proposed so far to explain the gap between observed and predicted HONO, including HONO formation by photolysis of o-nitrophenol (Bejan et al., 2006; Yang et al., 2021a), and the reaction of NO_2 with $HO_2 \cdot H_2O$ (Li et al., 2014b). But they have

75 yet to be confirmed to occur in the atmosphere, and are unlikely to be the main HONO source.

$$NO + OH \rightarrow HONO \tag{R2}$$
$$2NO_2 + H_2O \rightarrow HONO + HNO_3(surface) \tag{R3}$$
$$NO_2 + red_{ads} \rightarrow HONO + ox_{ads} \tag{R4}$$

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Heterogeneous reactions of NO_2 on various surfaces have drawn substantial interest due to the observed correlation between HONO and NO_2 during many field observations. Vertical gradient observations suggest that HONO is more likely produced from the ground surface (Wong et al., 2012; Kleffmann et al., 2003; Stutz et al., 2002; VandenBoer et al., 2013; Wong et al., 2011; Villena et al., 2011), while some observations found a good correlation between HONO and aerosol surface area

85 (Reisinger, 2000; Su et al., 2008a; Jia et al., 2020; Zheng et al., 2020; Liu et al., 2014), which can be related to the concentration and composition of particulate matter (Cui et al., 2018; Liu et al., 2014; Colussi et al., 2013; Yabushita et al., 2009; Kinugawa et al., 2011). Both laboratory studies and field observations have found that hydrolysis of NO_2 on wet surfaces can produce HONO (R3), and the uptake coefficient of NO_2 (γ) can vary by several orders of magnitude (Finlayson-Pitts et al., 2003; Stutz et al., 2004; Acker et al., 2004). HONO can also be generated by NO_2 reduction on various surfaces

90 (soot, semivolatile organic compounds, humic acid, etc.) at a much faster rate than NO_2 hydrolysis, but the surfaces could be inactivated in a short period of time (Ammann et al., 1998; Han et al., 2017a; Han et al., 2017b; Gerecke et al., 1998; Monge et al., 2010; Gutzwiller et al., 2002; Wall and Harris, 2017; Stemmler et al., 2006; Aubin and Abbatt, 2007). However, irradiation could enhance the reaction and maintain the activity of the surfaces, making it possible to play an important role in HONO formation during daytime. Both laboratory and field studies found that photolysis of adsorbed HNO_3 and

95 particulate nitrate (NO_3^-) could produce HONO (Ye et al., 2016; Ye et al., 2017; Zhou et al., 2003; Zhou et al., 2002b; Zhou et al., 2011), which might be an important HONO source, at least in remote areas and polar regions. Evidence of other new pathways and mechanisms has also been found and their atmospheric relevance discussed (Ge et al., 2019; Wang et al., 2016; Xu et al., 2019; Li et al., 2018b; Xia et al., 2021; Zhao et al., 2021; Gen et al., 2021).

100 The Pearl River Delta (PRD) region is one of the biggest city clusters in the world with dense population and large anthropogenic emissions. Rapid economic development and urbanization have led to severe air pollution in this region, which has been characterized by atmospheric "compound pollution" with concurrently high fine particulate matter ($PM_{2.5}$) and ozone (O_3) (Tang, 2004; Chan and Yao, 2008; Yue et al., 2010; Wang et al., 2017b; Xue et al., 2014; Zheng et al., 2010). Over recent years, O_3 has been increasing along with reduced $PM_{2.5}$ in the region (Li et al., 2014a; Liao et al., 2020; Wang et

105 al., 2009; Zhong et al., 2013; Lu et al., 2018), and has become the dominant factor of the air quality index exceeding the national standard (Feng et al., 2019), indicating the enhancement of atmospheric oxidation capacity. So far, two comprehensive atmospheric observations have been conducted in the PRD region, focusing on the balance and dynamics of OH sources and sinks (Hofzumahaus et al., 2009; Tan et al., 2019). Substantial amount of HONO was suggested to be a major source of the $OH–HO_2–RO_2$ radical system in these two campaigns (Lu et al., 2012; Tan et al., 2019) as well as in

110 other previous campaigns (Hu et al., 2002; Su et al., 2008b; Su et al., 2008a; Qin et al., 2009; Li et al., 2012; Shao et al., 2004).

In this work, we performed continuous measurements of HONO, along with trace gases, photolysis frequencies and meteorological conditions at an urban site in Guangzhou from 27 September to 9 November 2018, as part of the field

115 campaign "Particles, Radicals, Intermediates from oxiDation of primary Emissions in Greater Bay Area" (PRIDE-GBA2018). Benefiting from numerous prior field observational studies in the PRD region, our study stands in a strong position to ensure high quality of data acquisition and analysis of HONO, along with a full suite of other chemical species, providing a unique and valuable opportunity to refine our knowledge of HONO sources and sinks, as well as the role of HONO in the photochemistry of O_3 and OH in such a region with extensive air pollution as well as rigorous emission control over recent

120 years.

Departing from the valuable knowledge and experiences gained from numerous previous HONO studies in the PRD region and around the world, we aim to draw useful and unique insights from a detailed analysis of our dataset in the context of a comprehensive review of previous data and findings, with special attention paid to reducing and/or characterizing the

125 uncertainties in parameterizations and their implications on the relative importance of various HONO sources and sinks. Specifically, (1) a high resolution (3 km × 3 km) NOx emission inventory for the Guangzhou city (Huang et al., 2021) was used to estimate the primary emission rates of NOx and HONO, which would reduce the uncertainty of HONO primary emission rate; (2) a wide range of possible parameter values have been evaluated for each source to quantify their strengths and rank their importance; (3) uncertainties associated with each source and other possible factors are discussed in detail.

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2 Experiment

2.1 Observation site

The sampling site (23.14° N, 113.36° E) is located in the Guangzhou Institute of Geochemistry Chinese Academy of Sciences (GIGCAS). The instruments were deployed in the cabin on the rooftop of a seven-story building (~ 40 m above the ground). The site is surrounded by residential communities and schools, with no industrial manufacturers or power plants around, representing a typical urban environment in the PRD region. The south China Expressway and Guangyuan Expressway, both with heavy traffic loading, are located at west and south of the site, with distances of about 300 m. As a result, the site often experienced local emissions from traffic. The location and surroundings of the site are shown in Fig. S1.

2.2 Measurements

HONO was measured by a custom-built LOPAP (LOng Path Absorption Photometer) (Heland et al., 2001; Kleffmann et al., 2006). More information about our custom-built LOPAP (including principle, quality assurance/quality control, instrument parameters and intercomparison) are introduced in supplement information.

In addition to HONO, NOx (NO + NO_2) was measured by a nitrogen oxides analyzer (Thermo Scientific, Model 42i), which used a NO-NOx chemiluminescence detector equipped with a molybdenum-based converter with the time resolution and detection limit of 1 min and 0.4 ppbv respectively. It should be noted that the molybdenum oxide (MoO) converters may also convert some NOz (= NOy - NOx) (e.g., HONO, peroxyacetyl nitrate (PAN), HNO_3, and so on.) species to NO and hence could overestimate the ambient NO_2 concentrations. The degree of overestimation depends on both air mass age and the composition of NOy. At our site that was greatly affected by fresh emissions, the relative interferences of NOz to NO_2 have been estimated to be around 10% (see supplement information), which is closed to the results of Xu et al. (2013) and negligible for our discussion of HONO budget. O_3 was measured by an O_3 analyzer (Thermo Scientific, Model 49i) via ultraviolet absorption method with the time resolution and detection limit of 1 min and 1 ppbv respectively. SO_2 was measured by SO_2 analyzer (Thermo Scientific, Model 43i) via pulsed fluorescence method with the time resolution and detection limit of 1 min and 0.5 ppbv respectively. CO was measured by a CO analyzer (Thermo Scientific, Model 48i) with the time resolution and detection limit of 1 min and 0.04 ppmv respectively. NH_3 was measured by laser absorption spectroscopy (PICARRO, G2508) with the precision of < 3 ppbv at 1 min. Gaseous HNO_3 was detected by a Time-Of-Flight Chemical Ionization Mass Spectrometer (Aerodyne Research Inc., TOF-CIMS) with a time resolution of 1 min. And particulate nitrate (NO_3^-) was measured by Time-Of-Flight Aerosol Mass Spectrometry (Aerodyne Research Inc., TOF-AMS) with a time resolution of 1 min. $PM_{2.5}$ was measured by a Beta Attenuation Monitor (MET One Instruments Inc., BAM-1020) with the time resolution and detection limit of 1 h and 4.0 μg m^{-3} respectively. The meteorological data, including temperature (T), relative humidity (RH) and wind speed and direction (WS, WD) were recorded by Vantage Pro2 Weather Station (Davis Instruments Inc., Vantage Pro2) with the time resolution of 1 min. Photolysis frequencies including

J(HONO), J(NO$_2$) and J(O^{1}D) were measured by a spectrometer (Focused Photonics Inc., PFS-100) with a time resolution of 1 min.

3 Results and discussion

3.1 Data overview

The time series of meteorological parameters and pollutants during the campaign are shown in Fig. 1. The HONO concentrations ranged from 0.02 to 4.43 ppbv with an average of 0.74 ± 0.70 ppbv. Table 1 summarizes the HONO observations reported in PRD region since 2002. HONO appears to have shown a decreasing trend in Guangzhou, as improvement of air quality in Guangzhou was witnessed during the past decade. Spikes of NO occurred frequently, even up to 134.8 ppbv, as a result of traffic emissions from two major roads near the site. The concentrations of NO$_2$, SO$_2$, NH$_3$ and PM$_{2.5}$ ranged from 5.4–102.0 ppbv, 0–6.3 ppbv, 2.8–7.8 ppbv and 4–109 μg m^{-3} respectively with the average values of 50.8 ± 17.2 ppbv, 1.9 ± 1.2 ppbv, 6.3 ± 2.7 ppbv, and 36 ± 16 μg m^{-3} respectively. The O$_3$ concentrations ranged from 0.3–149.8 ppbv with an average peak concentration of 73.9 ± 28.4 ppbv. During the observation, the temperature ranged from 17 °C to 30 °C with an average of 24 ± 3 °C, and the relative humidity ranged from 28% to 97% with an average of 70 ± 17%. The average wind speed was 6.8 ± 4.5 m s^{-1}, while the maximum wind speed was 22.7 m s^{-1}. There was a pollution period from 8th to 10th October with elevated PM$_{2.5}$ (60 ± 12 μg m^{-3}) and HONO (0.94 ± 0.58 ppbv). By contrast, from 29 October to 3 November, efficient ventilation driven by strong winds (> 11 m s^{-1}) led to low levels of most pollutants in this period, with average concentrations of PM$_{2.5}$ and HONO at 28 ± 11 μg m^{-3} and 0.56 ± 0.34 ppbv, respectively.
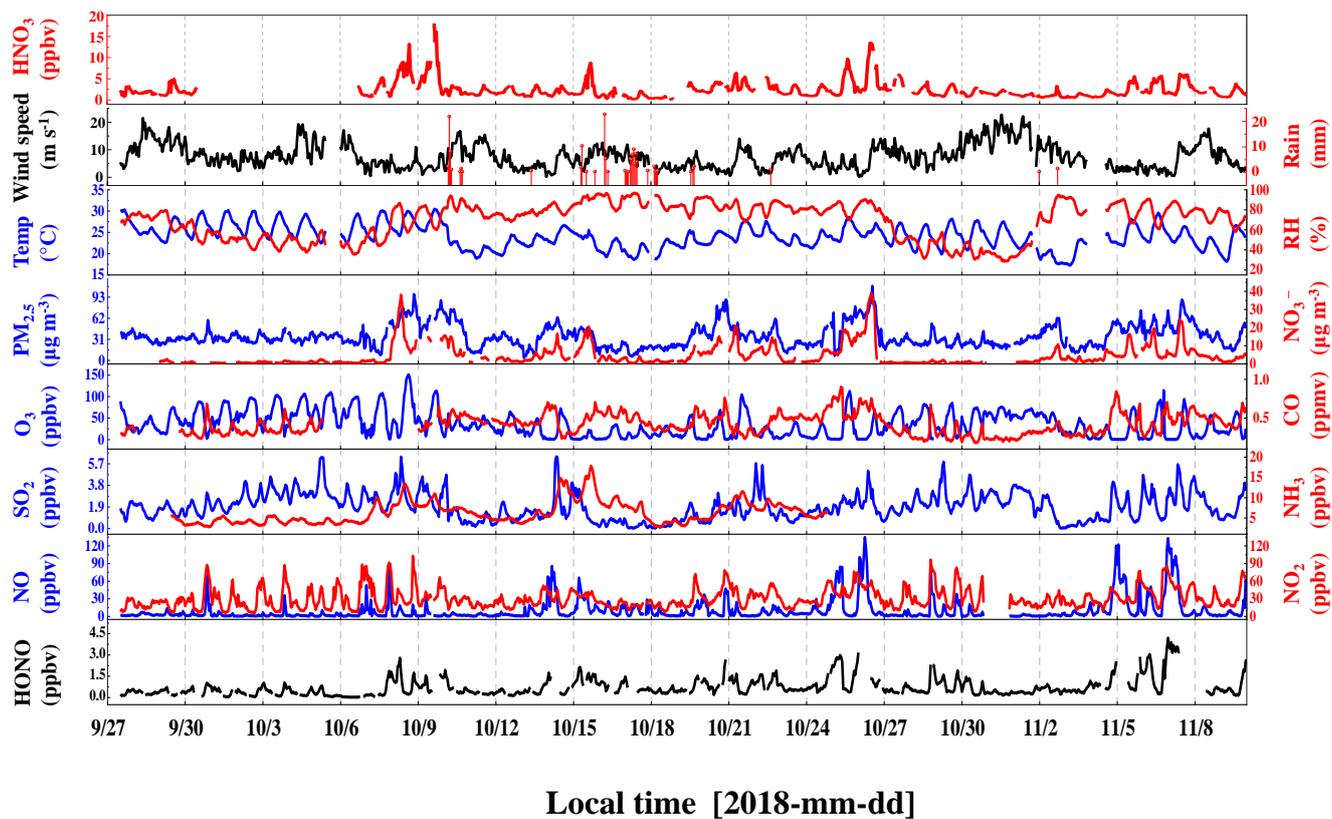
Figure 1. Temporal variations of meteorological and pollutants during the observation period.

Table 1. Overview of the ambient HONO, NO_2 and NOx measurement, as well as the ratios of $HONO/NO_2$ in the PRD region ordered chronologically. Data from Guangzhou are in italic.

Location	Date	HONO (ppbv)	HONO (ppbv)	NO_2 (ppbv)	NO_2 (ppbv)	NOx (ppbv)	NOx (ppbv)	$HONO/NO_2$	$HONO/NO_2$	Reference
		Night	Day	Night	Day	Night	Day	Night	Day	
Guangzhou (China)	*Jul 2002*	*1.89*	*–*	*–*	*–*	*–*	*–*	*–*	*–*	*1*
	Nov 2002	*1.52*	*–*	*–*	*–*	*–*	*–*	*–*	*–*	
Xinken (China)	*Oct–Nov 2004*	*1.20*	*1.30*	*0.80*	*34.8*	*30.0*	*37.8*	*40.0*	*0.037*	*0.027*	*2*
Back Garden (China)	*Jul 2006*	*0.93*	*0.95*	*0.24*	*16.5*	*4.5*	*20.9*	*5.5*	*0.057*	*0.053*	*3*
Guangzhou (China)	*Jul 2006*	*2.80*	*3.50*	*2.00*	*20.0*	*30.0*	*–*	*–*	*0.175*	*0.067*	*4*
Guangzhou (China)	*Oct 2015*	*1.64*	*2.25*	*0.90*	*40.5*	*27.3*	*57.9*	*39.8*	*0.060*	*0.030*	*5*
Guangzhou (China)	*Jul 2016*	*1.03*	*1.27*	*0.70*	*35.0*	*25.9*	*66.3*	*52.1*	*0.040*	*0.070*	*6*
Guangzhou (China)	*Sep–Nov 2018*	*0.74*	*0.91*	*0.44*	*36.9*	*23.3*	*47.7*	*30.1*	*0.026*	*0.022*	*–*
Jiangmen (China)	Oct–Nov 2008	0.60	–	0.48	–	–	–	9.1	–	–	7
Hong Kong (China)	Aug 2011	0.66	0.66	0.70	21.8	18.1	29.3	29.3	0.031	0.042	8
	Nov 2011	0.93	0.95	0.89	27.2	29.0	37.2	40.6	0.034	0.030	
	Feb 2012	0.91	0.88	0.92	22.2	25.8	37.8	48.3	0.036	0.035	
	May 2012	0.35	0.33	0.40	14.7	15.0	19.1	21.1	0.022	0.030	
Hong Kong (China)	Sep–Dec 2012	0.13	–	–	–	–	–	–	–	–	9
Heshan (China)	Oct 2013	1.57	–	–	–	–	–	–	–	–	10
Heshan (China)	Oct–Nov 2014	1.40	1.78	0.77	19.3	17.9	21.5	22.7	0.093	0.055	11
Hong Kong (China)	Mar–May 2015	3.30	2.86	3.91	–	–	–	–	–	–	12
Heshan (China)	Jan 2017	2.70	3.10	2.30	–	–	–	–	0.116	0.089	13

185 **References:1: Hu et al. (2002); 2: Su et al. (2008a) and Su et al. (2008b); 3: Su (2008) and Li et al. (2012); 4: Qin et al. (2009); 5: Tian et al. (2018); 6: Yang et al. (2017a); 7: Yang (2014); 8: Xu et al. (2015); 9: Zha et al. (2014); 10: Yue et al. (2016); 11: Liu (2017); 12: Yun et al. (2017); 13: Yun (2018).**

The time series of photolysis frequencies J(HONO), J(O^{1}D) and J(NO$_2$) in the whole observation period are shown in Fig. S3.
The maximum values of J(HONO), J(O^{1}D) and J(NO$_2$) are 1.58×10^{-3} s^{-1}, 2.54×10^{-5} s^{-1} and 9.31×10^{-3} s^{-1}, respectively. These J values tracked a similar diurnal pattern, reaching a maximum at noon with high solar radiation and decreasing to zero at night.

The diurnal variations of HONO, NO$_2$, HONO/NO$_2$, and NO are shown in Fig. 2. A daytime trough and a night-time peak of HONO were observed, as typically seen at urban and rural sites (Lee et al., 2016; Xue et al., 2020; Villena et al., 2011; Yang et al., 2021b). The observed high HONO concentration around 0.5 ppbv at daytime implies strong HONO production to balance its rapid loss through photolysis. NO$_2$ showed a similar diurnal pattern. It is worth noting that the diurnal variation of NO was quite similar to that of HONO, implying the potential association between them. Additionally, the observed large amount of NO (10.8 ± 17.2 ppbv) at night indicated strong primary emission near the site. As an indicator of NO$_2$ to HONO conversion, the ratio of HONO/NO$_2$ rose at night and decreased after sunrise due to photolysis, ranging from 0.002 to 0.091 with an average of 0.023 ± 0.013, which is lower than most previous field observations in the PRD region (Li et al., 2012; Qin et al., 2009; Xu et al., 2015), and is typical for relatively fresh plumes (Febo et al., 1996; Lammel and Cape, 1996; Sörgel et al., 2011b; Stutz et al., 2004; Zhou et al., 2007; Su et al., 2008a).
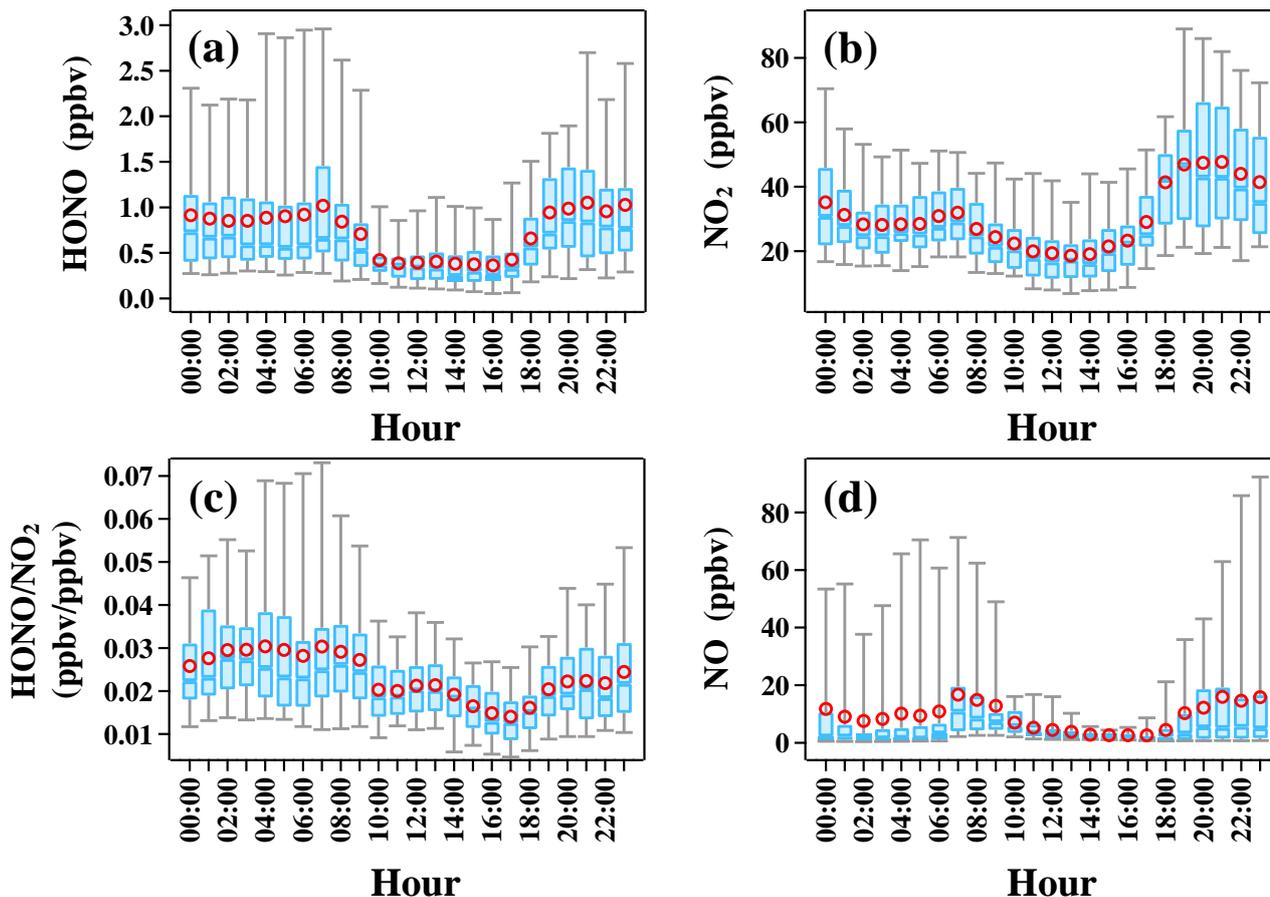
Figure 2. Diurnal profiles of (a) HONO, (b) NO₂, (c) HONO/NO₂ and (d) NO during the observation period. The blue line in the box and red circle refer to the median and mean, respectively. Upper and lower boundaries of the box represent the 75th and the 25th percentiles; the whiskers above and below each box represent the 95th and 5th percentiles. The box plots presented in this study is generated by an Igor Pro-based computer program, Histbox (Wu et al., 2018).

3.2 Nocturnal HONO sources and sinks

3.2.1 Direct emissions

As noted in Sect. 2.1, the site was expected to receive substantial direct emission of HONO from two major roads nearby. We obtained the emitted HONO/NOx ratios in fresh plumes defined with the following criteria (Xu et al., 2015): (a) NOx > 49.7 ppbv (highest 25% of NOx data); (b) NO/NOx > 0.8; (c) good correlation between NOx and HONO ($R^2 > 0.70$, $P <$ 0.05); (d) short duration of plumes (< 2 h); (e) global radiation < 10 W m⁻² ($J(NO_2) < 0.25 \times 10^{-3}$ s⁻¹).

During the campaign, 11 fresh plumes were identified to satisfy all of the criteria (see Table S2). Two cases among them are shown in Fig. S4. The HONO/NOx ratios in these selected plumes varied from 0.1% to 1.5% with an average value of 0.9 ± 0.4%, which is comparable to the average value of 1.2% (Xu et al., 2015) and 1.0% (Yun et al., 2017) measured in Hong Kong, 0.79% measured in Nanjing (Liu et al., 2019b) and 0.69% observed in Changzhou (Shi et al., 2020). It should be noted that the emission factor derived in this study was based on field observation and the screening criterion for fresh air mass was NO/NOx > 0.8, while the fresh air mass was characterized by NO/NOx > 0.9 in the tunnel experiments conducted by Kurtenbach et al. (2001), so the air masses we selected were still slightly aged and the emission factor derived in this study is slightly overestimated.

To quantify the primary emission rate of HONO, three methods have been used in previous studies (Liu et al., 2019b; Liu et al., 2020a; Meng et al., 2020). In method (1), the observed NOx concentration is assumed to represent the accumulation of emissions but ignore the sinks of NOx and HONO, as well as transport and convection. On this basis, [HONO]$_{emis}$ (the primary emission's contribution to HONO concentration) is estimated as the product of emission coefficient K and observed NOx concentration (Cui et al., 2018; Huang et al., 2017) (see Eq. (1)). Since it is difficult to determine the time of NOx emissions, method (1) can not exclude the NOx levels before emission begins. With this in mind, in method (2), primary emission rate P$_{emis}$ is estimated as the product of emission coefficient K and [ΔNOx]/Δt, where [ΔNOx] is the difference between observed NOx at two time points (Liu et al., 2019b; Zheng et al., 2020) (see Eq. (2)). Obviously, it can only be used when NOx is increasing. It should be noted that any loss of NOx and HONO can be a source of error for these two methods, especially during daytime. In method (3), primary emission rate P$_{emis}$ is equal to the product of emission coefficient K and NOx*, the NOx emission from source emission inventory (Michoud et al., 2014; Su et al., 2008b) (see Eq. (3)). This method adheres to the definition of HONO emission rate, assuming that the primary sources are evenly mixed in a specific area. It is desirable to use emission inventory data with high spatial and temporal resolution to obtain an accurate estimate.

$$[HONO]_{emis} = K \times [NOx] \tag{1}$$

$$P_{emis} = K \times [\Delta NOx]/\Delta t \tag{2}$$

$$P_{emis} = K \times NOx^* \tag{3}$$

$$P_{HONO} = \frac{[HONO]_{t_2} - [HONO]_{t_1}}{t_2 - t_1} \tag{4}$$

In this study, we first used NOx emission rate from a high-resolution emission inventory (Huang et al., 2021) to calculate emission rate of HONO P$_{emis}$ at night (18:00–6:00). The NOx emission rate was extracted from a 3 km × 3 km grid cell centred around our site. As a comparison, we also used the 2017 NOx emission inventory of Guangzhou city to repeat the calculation. The two inventories are primarily different in spatial resolution. The high-resolution 3 km × 3 km data is expected to better represent local traffic emissions, whereas the city-level emission inventory represents the total emission.

Since we cannot quantify the relative contribution of the local and regional emissions to this site, two results are used to represent upper and lower limits of the contribution of primary emissions to HONO. The nighttime height of the boundary layer is assuming to 200 m according to the previous study in the PRD region in autumn by Fan et al. (2008).

The observed HONO accumulation rate P_{HONO} is calculated by Eq. (4), where $[HONO]_{t_1}$ and $[HONO]_{t_2}$ represent the HONO concentration at 18:00 and 6:00 Local Time, respectively. Then an average P_{HONO} of 0.02 ± 0.06 ppbv h^{-1} can be derived. Hourly HONO primary emission rates calculated with the two inventories are shown in Fig. 5 (a). P_{emis} calculated with the high-resolution emission data (3 km × 3 km) shows a steep downward trend from 18:00 (0.56 ppbv h^{-1}) to 4:00 (0.14 ppbv h^{-1}), followed by an upward trend from 4:00 (0.14 ppbv h^{-1}) to 6:00 (0.25 ppbv h^{-1}) with the average of 0.30 ± 0.15 ppbv h^{-1}. By contrast, P_{emis} with the city level emission data (Guangzhou) is much lower (0.04 ± 0.02 ppbv h^{-1}) and varied smoothly throughout the night. Similar results have been obtained at urban sites (Liu et al., 2020a; Liu et al., 2020b; Gu et al., 2021) and a suburban site (Michoud et al., 2014), while the result at a rural site is much lower (Su et al., 2008b) in the PRD region. The uncertainty of P_{emis} stems from the uncertainty of the inventories (-25%–28%) (Huang et al., 2021). Regardless, direct emission of HONO represents a large HONO source at night along with other sources of HONO that remain to be considered.

We also calculated the primary emission's contribution to HONO ($[HONO]_{emis}/[HONO]$) using Method (1) and made comparisons against $[HONO]_{emis}/[HONO]$ ratios obtained previously from urban sites in China (Table S3). The values varied widely from 12% to 52%, with seasonal difference of more than a factor of 2 for the same site, reflecting large variability of HONO emissions spatially and temporally. In comparison, the ratio of $[HONO]_{emis}/[HONO]$ at our site is relatively high at 47%, as can be expected from the relatively strong vehicle exhaust emissions near our site.

In addition to traffic emissions, we also estimated the HONO emission rate from soil P_{soil} (ppbv h^{-1}) according to Eq. (5) (Liu et al., 2020a):

$$P_{soil} = \frac{\alpha\, F_{soil}}{H} \tag{5}$$

where F_{soil} is the emission flux (g m^{-2} s^{-1}); H is the height of boundary layer (m) and was assumed to be 200 m (Fan et al., 2008); α is the conversion factor ($\alpha = \frac{1 \times 10^9 \times 3600 \times R \times T}{M \times P} = \frac{2.99 \times 10^{13} \times T}{M \times P}$); T is the temperature (K); M is the molecular weight (g mol^{-1}) and P is the atmospheric pressure (Pa). HONO emission flux from soil depends on the temperature, water content and nitrogen nutrient content of soil, which have been considered according to the parameters reported in the literature (Oswald et al., 2013). Since grassland, coniferous forest and tropical rain forest are the typical plants in Guangzhou city area (Wu et al., 2015) and their emission fluxes are comparable (Oswald et al., 2013), emission flux from grassland was adopted to represent the soil HONO emission in Guangzhou. The average nighttime P_{soil} varied from 0.011 to 0.035 ppbv h^{-1}, with a mean value of 0.019 ± 0.009 ppbv h^{-1}. The HONO emission rate from soil at our site is slightly larger than the result reported in Shijiangzhuang urban area (Liu et al., 2020a) and comparable to that in Beijing urban area (Liu et al., 2020b). A

caveat is that the calculation relies on laboratory results and is therefore prone to errors due to any possible inconsistency between laboratory simulations and field observations. Overall, soil emission is a minor source compared to other sources.

3.2.2 NO + OH homogeneous reaction

285 The reaction between NO and OH acts as the most well known homogenous HONO source. It can contribute a substantial fraction to HONO formation when NO and OH concentrations are high (Alicke et al., 2003; Liu et al., 2019b; Wong et al., 2011; Tong et al., 2015; Zhang et al., 2019). Taking the homogeneous Reactions R2 and R5 into account, the net HONO homogeneous production rate can be calculated following Eq. (6):

290 $$NO + OH \rightarrow HONO \tag{R2}$$

$$HONO + OH \rightarrow NO_2 + H_2O \tag{R5}$$

$$P_{OH+NO}^{net} = k_{NO+OH}[NO][OH] - k_{HONO+OH}[HONO][OH] \tag{6}$$

In Eq. (6), k_{NO+OH} (7.2×10^{-12} cm^3 s^{-1}) and $k_{HONO+OH}$ (5.0×10^{-12} cm^3 s^{-1}) are the reaction rate constants of the Reactions
295 R2 and R5 at 298 K, respectively (Li et al., 2012). Since the OH concentration was not measured, an average nighttime value of 0.5×10^6 cm^{-3} measured in Heshan in the PRD region in autumn of 2014 was assumed (Tan et al., 2019). As shown in Fig. 3, the variation of P_{OH+NO}^{net} largely followed that of NO, since the concentration of NO was 10 times larger than HONO. And the average value of P_{OH+NO}^{net} is 0.13 ± 0.30 ppbv h^{-1}, leading to a cumulative HONO contribution of 1.62 ppbv. The obtained P_{OH+NO}^{net} is similar to previous studies, such as 0.12 ppbv h^{-1} in Xianyang (Li et al., 2021), 0.13 ppbv h^{-1} in Zhengzhou (Hao
300 et al., 2020), 0.26 ppbv h^{-1} in Xi'an (Huang et al., 2017) and 0.28 ppbv h^{-1} in Guangzhou Back Garden (Li et al., 2012). We note that the measured HONO only increased 0.26 ppbv in this period, much smaller than the cumulative production of HONO by the reaction between NO and OH, indicating a large sink to balance this source and other sources that will be discussed below.

305 Since OH was not measured in our study, we carried out sensitivity tests using one fifth and twice of assumed OH concentration (0.5×10^6 cm^{-3}) (Lou et al., 2010). As shown in Table S4, within the range of nighttime OH concentration, the cumulative production of the homogeneous reaction of NO + OH in this study are always large enough to surpass the average measured accumulation of HONO, indicating that the NO + OH source is a major source term regardless of uncertainties in OH concentrations.

310
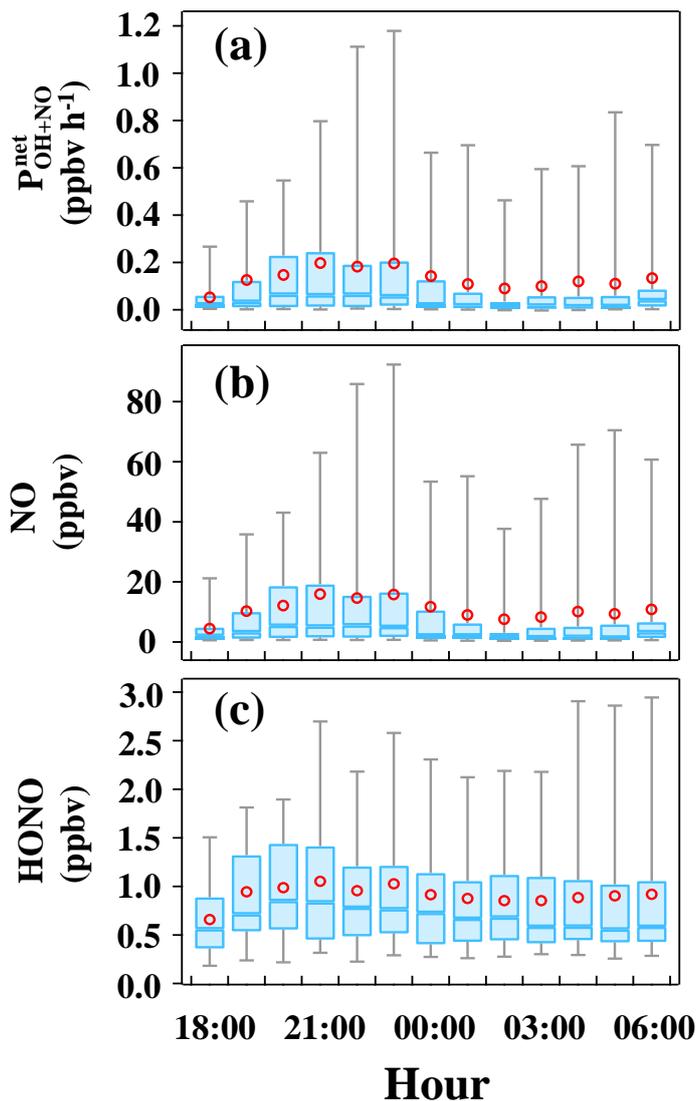
Figure 3. The mean nocturnal variation of (a) P_{OH+NO}^{net}, (b) NO and (c) HONO. The blue line in the box and red circle refer to the median and mean, respectively. Upper and lower boundaries of the box represent the 75th and the 25th percentiles; the whiskers above and below each box represent the 95th and 5th percentiles.

3.2.3 NO₂ to HONO heterogeneous conversion

Our analysis so far suggests that direct emissions and the homogeneous reaction between NO and OH are two major sources of HONO at night. This finding is in line with the relatively high correlation ($R^2 = 0.5927$) between HONO and NO (Fig. 4 (a)). In the following, we present results from correlation analysis to explore possible pathways of heterogeneous NO₂ to HONO conversion at night (18:00–6:00).

The ratio of HONO/NO$_2$ has often been used to indicate the heterogeneous conversion efficiency of NO$_2$ to HONO (Lammel and Cape, 1996; Stutz et al., 2002), for being less influenced by transport processes or convection. Figure 4 (c) shows a weak correlation (R^2 = 0.0638) between HONO/NO$_2$ and PM$_{2.5}$, suggesting that the formation of HONO on aerosol surfaces might not be the main pathway (Kalberer et al., 1999; Kleffmann et al., 2003; Wong et al., 2011; Zhang et al., 2009; Sörgel et al., 2011a; VandenBoer et al., 2013). Because the surface area of ground (including vegetation surface, building surface and soil, etc.) is generally larger than the surface area of aerosols, some studies suggested that the heterogeneous reaction of NO$_2$ and water vapor on ground surfaces was the main source of HONO (Harrison and Kitto, 1994; Li et al., 2012; Wong et al., 2012). Furthermore, the correlations between HONO/NO$_2$ and NH$_3$ and RH are 0.3746 and 0.2381, respectively, and the correlation further improved between HONO/NO$_2$ and the product of NH$_3$ and RH (R^2 = 0.4597). Some studies proposed that NH$_3$ can decrease the free-energy barrier in hydrolysis of NO$_2$ thus enhance the HONO formation (Xu et al., 2019; Li et al., 2018b; Wang et al., 2021a).
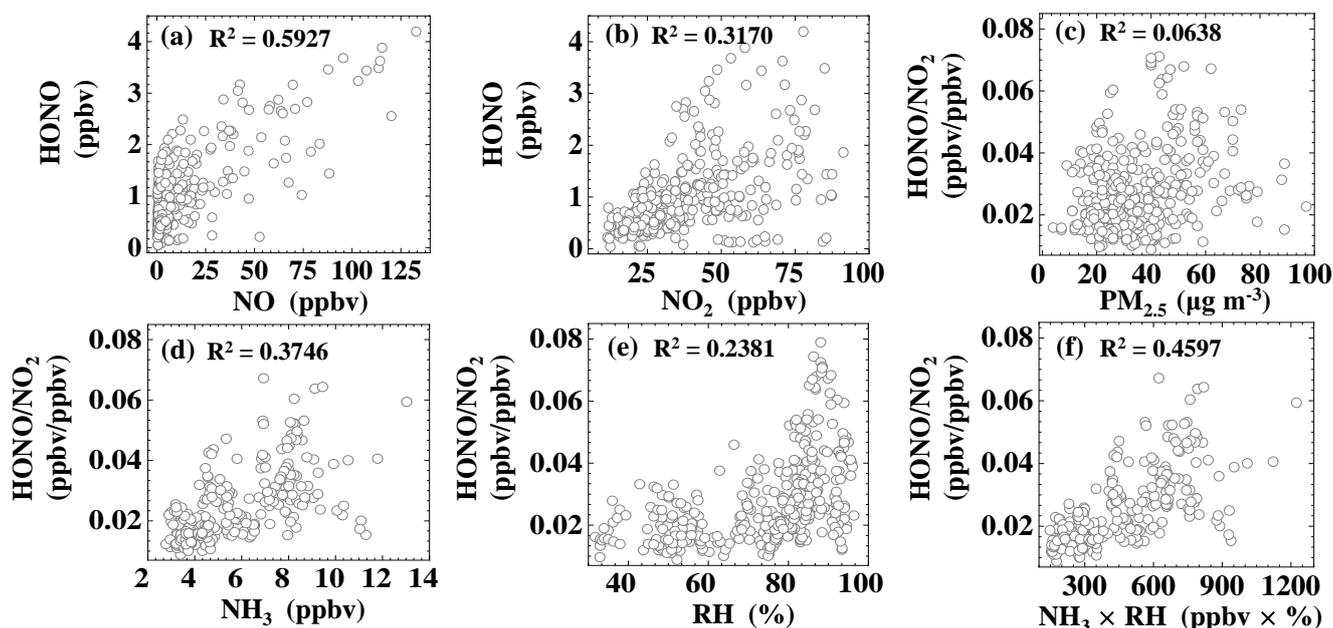
Figure 4. Correlations between HONO, HONO/NO$_2$ and various parameters during the time interval of 18:00–6:00.

In Fig. S5, we further explored the RH effect by focusing on high HONO/NO$_2$ values, i.e., the 5 highest HONO/NO$_2$ values for 5% RH intervals (Stutz et al., 2004). When RH was lower than 87.5%, HONO/NO$_2$ increased with RH, which is in accordance with the reaction kinetics of disproportionation reaction of NO$_2$ and H$_2$O. Furthermore, the slope of linear fitting between HONO/NO$_2$ and RH was much smaller for RH range of 30% ~ 70% (slope = 0.04%; R^2 = 0.5202) than for the RH range of 70% ~ 87.5% (slope = 0.25%, R^2 = 0.8767). Similar piecewise correlations between HONO/NO$_2$ and RH have been found in previous studies (Qin et al., 2009; Zhang et al., 2019), which have been interpreted as evidence for the non-linear dependence of NO$_2$-to-HONO conversion efficiency on RH. Once the relative humidity exceeded 87.5%, NO$_2$-to-HONO

conversion appeared to be inhibited by RH (slope = -0.32%; R^2 = 0.9750). A possible explanation is that the number of water layers formed on various surfaces increased rapidly with RH, resulting in effective uptake of HONO and making the surface inaccessible or less reactive to NO_2. Previous studies also found fast growth of aqueous layers when RH over 70% for glass (Saliba et al., 2001) and over 80% for stone (Stutz et al., 2004). The tipping point inferred from ambient observations appear

345 to vary across locales, likely reflecting the different composition of the ground surfaces, e.g., 60% for Chengdu (Yang et al., 2021b), 65–70% for Beijing (Wang et al., 2017a), 70% for Back Garden (Li et al., 2012), 75% for Shanghai (Wang et al., 2013), and 85% for Xi'an (Huang et al., 2017).

We calculated the strength of the HONO formation from NO_2 heterogenous reaction on on ground surface (P_{ground}) and

350 aerosol surface ($P_{aerosol}$) based on the empirical data derived from either experiments or observations.

$$P_{ground} = \frac{1}{8}\, \gamma_{NO_2 \rightarrow ground} \times [NO_2] \times C_{NO_2} \times \frac{S_g}{V} \tag{7}$$

$$P_{aerosol} = \frac{1}{4}\, \gamma_{NO_2 \rightarrow aerosol} \times [NO_2] \times C_{NO_2} \times \frac{S_a}{V} \tag{8}$$

$$\frac{S_g}{V} = \frac{2.2}{H} \tag{9}$$

Where C_{NO_2} is the mean molecular velocity of NO_2 (m s^{-1}), $\gamma_{NO_2 \rightarrow ground}$ and $\gamma_{NO_2 \rightarrow aerosol}$ represent the uptake coefficient of

355 NO_2 on ground surface and aerosol surface, respectively, S_g/V and S_a/V are the surface area to volume ratio (m^{-1}) for both ground and aerosol, respectively. Considering the land use type of the study site, we treated the ground as an uneven surface, and a factor of 2.2 per unit ground surface measured by Voogt and Oke (1997) was adopted to calculate the total active surface. Hence, S_g/V can be calculated by Eq. (9), where H is the mixing layer height. The surface area-to-volume ratio S_a/V of PM_{10} was not avaliable in this study and was estimated according to $PM_{2.5}$ and S_a/V value in Guangzhou Xinken by Su et

360 al. (2008a). The uptake coefficients of NO_2 on ground surface and aerosol surface were assumed to be 4×10^{-6} following previous studies (Li et al., 2018a; Liu et al., 2019a; Zhang et al., 2021) (the summary of the parameterisations used for nighttime HONO budget calculation can be found in Table S5). With these assumptions, an average value of P_{ground} of 0.27 ± 0.13 ppbv h^{-1} can be derived, which is far larger than $P_{aerosol}$ (0.03 ± 0.02 ppbv h^{-1}) (Fig. 5 (c) and (d)).

365 In sum, our correlation analysis for HONO/NO_2 and parameterized calculations suggested that nighttime heterogenous conversion of NO_2 into HONO at our site maily occured on the ground rather than on aerosol sources, while the correlation analysis provides evidence for the role of NH_3 and water vapor in HONO formation. It should be noted that, unlike the NO + OH reaction or the primary emission, which turned out as major HONO sources even at their lower limit considering uncertainties, the magnitude of the heterogenous source as well as its contribution to overall HONO budget varied greatly

370 with the assumed uptake coefficients of NO_2, which can span two orders of magnitude.

3.2.4 Removal of HONO

As discussed above, strong sinks are required to balance the nighttime HONO production. Since the reactions of HONO + OH and HONO + HONO are negligible (Kaiser and Wu, 1977; Mebel et al., 1998), it is conceivable that nighttime HONO is mainly removed through deposition L_{Dep} (El Zein and Bedjanian, 2012; Li et al., 2012; Hao et al., 2020; Meng et al., 2020), transport processes, e.g. entrainment of background air $L_{dilution}$ (Gall et al., 2016; Meng et al., 2020), and uptake on aerosols $L_{aerosol}$. These terms can be expressed as follows:

$$L_{Dep} = \frac{V_d \times [HONO]}{H} \tag{10}$$

$$L_{aerosol} = \frac{1}{4} \, \gamma_{HONO \rightarrow aerosol} \times [HONO] \times C_{HONO} \times \frac{S_a}{V} \tag{11}$$

$$L_{dilution} = k_{(dilution)} \times ([HONO] - [HONO]_{background}) \tag{12}$$

where V_d is the average deposition velocity, $\gamma_{HONO \rightarrow aerosol}$ is the uptake coefficient of HONO on aerosol surface, $k_{(dilution)}$ is the dilution rate (including both vertical and horizontal transport) (Dillon et al., 2002). C_{HONO} is the mean molecular velocity of HONO (m s^{-1}), and [HONO] and [HONO]$_{background}$ represents the HONO concentration at the observation site and the background site, respectively. In this work, the lowest nighttime HONO concentration was taken as the [HONO]$_{background}$.

The average loss rate of HONO by dilution was calculated to be 0.18 ± 0.16 ppbv h^{-1}, which is in the range of prior results (Gall et al., 2016; Liu et al., 2020a; Liu et al., 2020b). The average value of $L_{aerosol}$ and $L_{OH+HONO}$ was 0.008 ± 0.006 ppbv h^{-1} and 0.008 ± 0.012 ppbv h^{-1}, respectively. In order to balance the nighttime HONO budget and assuming dry deposition to be responsible for the remaining amount of HONO loss, a dry deposition rate of ~ 2.5 cm s^{-1} was adopted accounting for an average loss rate of 0.41 ± 0.31 ppbv h^{-1} by deposition between 18:00–6:00, when using the median parameter values in Table S5 to calculate the HONO sources and sinks. This result is consistent with previous studies suggesting dry deposition as the dominant loss way for HONO during night (Li et al., 2012; Hao et al., 2020; Meng et al., 2020; VandenBoer et al., 2013). The upper limit of $L_{aerosol}$ is only 0.10 ± 0.08 ppbv h^{-1}, suggesting that HONO loss on aerosols was not a major sink, as also suggested by prior studies (El Zein and Bedjanian, 2012; El Zein et al., 2013; Romanias et al., 2012).

3.2.5 Nighttime HONO budget: relative importance of sources and their uncertainties

It is useful to evaluate the balance of HONO budget by evaluating calculated/parameterized sources and sinks against the observed HONO level and variability. The observed production rate of HONO P_{obs} can be defined as the sum of the total loss rates and change rates of HONO (Gu et al., 2021). When using the median values of parameters (Table S5) and taking an average throughout the night (18:00–6:00), all five sources are greater than or close to the average accumulating rate of

HONO at night derived from observed HONO variation (0.02 ± 0.06 ppbv h^{-1}), indicating a balanced HONO budget considering all uncertainties. Ranking the source strengths with their median estimates suggested that heterogeneous conversion of NO$_2$ on ground surface (0.27 ± 0.13 ppbv h^{-1}), primary emission from vehicle exhaust (between 0.04 ± 0.02 ppbv h^{-1} and 0.30 ± 0.15 ppbv h^{-1} with a middle value of 0.16 ± 0.07 ppbv h^{-1}) and the homogeneous reaction of NO + OH (0.14 ± 0.30 ppbv h^{-1}) were major sources of HONO at night. Nighttime soil emission rate (0.019 ± 0.009 ppbv h^{-1}) and heterogeneous NO$_2$ conversion on the aerosol surfaces (0.03 ± 0.02 ppbv h^{-1}) were two other minor sources. Dry deposition (0.41 ± 0.31 ppbv h^{-1}) was the principal loss process of nighttime HONO, followed by dilution (0.18 ± 0.16 ppbv h^{-1}), while the homogeneous reaction of HONO + OH (0.008 ± 0.012 ppbv h^{-1}) and HONO uptake on the aerosol surfaces (0.008 ± 0.006 ppbv h^{-1}) were insignificant.

We also made an attempt to obtain a time resolved HONO budget on an hourly basis, although the results are not satisfactory for all the hours at night, with obvious differences between observed and calculated rates of HONO variation, e.g., at 22:00 and from 2:00 to 5:00 (Fig. S6). This is well expected considering much more amplified uncertainties associated with hourly variabilities of various quantities, which can be considerably reduced by averaging all hours. This is why subtle and careful data filtering is necessary when nightime HONO chemistry is examined in detail (Wong et al., 2011). Such a granular analysis is more appropriate for the daytime when HONO lifetime is much shorter and uncertainties affecting the interpretation of HONO chemistry (e.g., emission and transport) are much muted. As a matter of fact, because the rate of HONO change shown in Fig. S6 is a first order derivative of the HONO concentration itself, one can expect that HONO concentrations from each source would show greater variations, making it more difficult to compare on an hourly basis. Another challenge is that since those parameters used for calculating HONO source strengths have a range in their estimates (Table S5), the HONO source strengths also have a wide range individually, and therefore there are numerous possible combinitions of these sources with different strengths and rankings to close the budget.

The comparison and ranking of sources considering variability and uncertainty becomes less straightforward than ranking nighttime average source strengths (Fig. 5). Among the three largest sources, both primary (non-soil) emission and NO$_2$ heterogenous source on ground showed an evening peak and decreased after midnight. The NO + OH source showed a different trend with its lowest level in the evening, making it the smallest source among the three at that time. Although the NO$_2$ heterogenous source on ground appeared the largest with its median parameter value, it also had the largest range of estimate, suggesting that its importance is more uncertain compared to the other sources. On the other hand, the other two minor sources, i.e., the NO$_2$ heterogenous source on aerosols and soil emission are substantially less important than these three sources given their ranges of low estimates. The variability and uncertainty of dry deposition are entirely dependant on other terms of sources and sinks since it is derived as a final term to balance the budget.
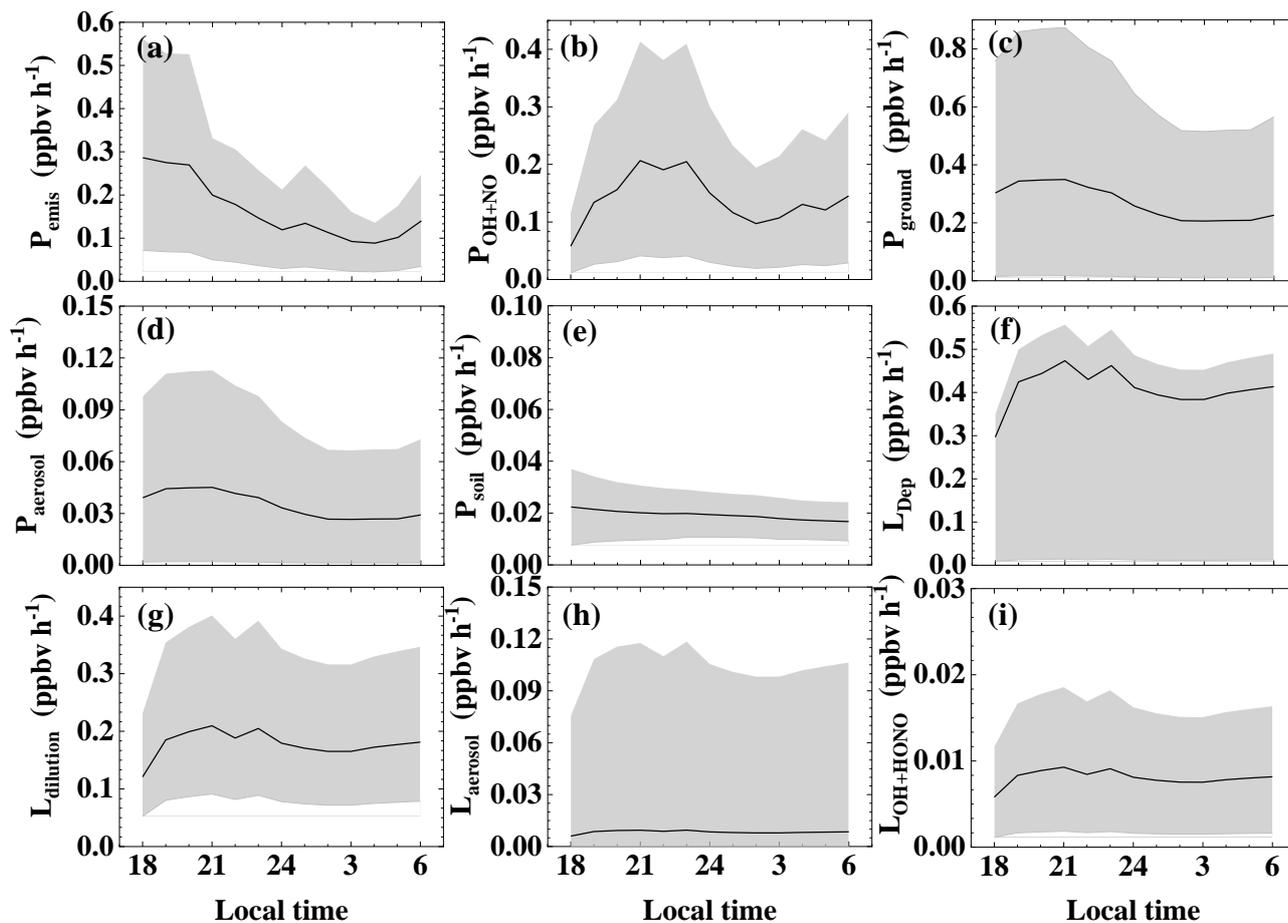
Figure 5. The nocturnal variation of the terms of HONO budget (a) primary emission from vehicle exhaust, (b) homogeneous reaction of NO + OH, (c) heterogeneous conversion of NO₂ on ground surfaces, (d) heterogeneous conversion of NO₂ on aerosol surfaces, (e) soil emission and HONO loss from (f) dry deposition, (g) dilution, (h) uptake on aerosols, (i) HONO + OH during Sep. 27–Nov. 9 2018 in Guangzhou. The black line is the HONO production rates with the median values of parameters, and the grey shadow represents their lower and upper limits.

3.3 Daytime HONO budget and unknown sources analysis

3.3.1 Budget analysis

In this section, we move on to a detailed budget analysis for HONO during the daytime, when chemistry is distinctly different from at night. Similar to the nighttime analysis by exploring different terms for the daytime chemistry, the time variation of HONO concentration at our site can be related to its sources and sinks as follows:

$$\frac{\partial[HONO]}{\partial t} = P_{HONO} - L_{HONO} = (P_{OH+NO} + P_{Unknown} + P_{emis} + P_{soil} + T_V + T_H) - (L_{OH+HONO} + L_{Phot} + L_{Dep}) \tag{13}$$

450

where $\partial[HONO]/\partial t$ represents the time variation of HONO; P_{HONO} and L_{HONO} are the sources and sinks of HONO, respectively; P_{OH+NO} and $L_{OH+HONO}$ are the homogeneous HONO formation and loss rates in Reactions R2 and R5, respectively; $P_{Unknown}$ is the HONO production rate from unknown sources; T_V and T_H are two terms representing vertical and horizontal transport processes, respectively; L_{Phot} denotes the photolysis loss rate of HONO, which can be calculated

455   with $L_{Phot} = J(HONO) \times [HONO]$; deposition loss rate of HONO L_{Dep} can be calculated by Eq. (10). Assuming a daytime V_d of 1.6 cm s^{-1} (Hou et al., 2016; Li et al., 2011) and a daytime mixing height (H) of 1000 m (Liao et al., 2018; Song et al., 2019), the average L_{Dep} is 0.003 ± 0.001 ppbv h^{-1}, three orders of magnitude smaller than L_{Phot} and therefore can be ignored in the following discussion.

460   OH was not measured and was calculated with a parameterized approach based on strong correlation between observed OH radicals and $J(O^1D)$. The parameterization was first proposed by Rohrer and Berresheim (2006) and has been applied by several studies in China (Lu et al., 2013; Lu et al., 2012; Lu et al., 2014). In this study, OH was estimated with observed $J(O^1D)$ along with parameters from fitting the observed OH radicals and $J(O^1D)$ data in Guangzhou Back Garden by Lu et al. (2012). The daytime maximum OH concentration was estimated to be 1.3×10^7 cm^{-3}, which is slightly smaller than the daily

465   peak values of 1.5–2.6×10^7 cm^{-3} observed in summer of Guangzhou by Lu et al. (2012). And the estimated daily average OH concentration is 6.7×10^6 cm^{-3}, close to 7.5×10^6 cm^{-3} measured in the PRD region in autumn of 2014 by Yang et al. (2017b). Daytime P_{emis} was calculated based on the method (3) (mentioned in Sect. 3.2.1). Because the HONO lifetime was in the order of 20 min under typical daytime conditions (Stutz et al., 2000) and the transport distance is only a few kilometers, the NOx emission rate extracted from the 3 km × 3 km grid cell centred around sampling site is used to calculate the impact

470   of primary emission on HONO.

To minimize interferences, we chose a period from 9:00 to 15:00 with intense solar radiation and a short HONO lifetime. Horizontal transport T_H was assumed negligible by selecting the cases with low wind speed (below 3 m s^{-1}) (Su et al., 2008b; Yang et al., 2014). The magnitude of vertical transport T_V can be estimated by using a parameterization for dilution by

475   background air according to Dillon et al. (2002), i.e. $T_V = k_{(dilution)} \times ([HONO] - [HONO]_{background})$. Where $k_{(dilution)}$ is the dilution rate, $[HONO]_{background}$ represents the background HONO concentration. Assuming a $k_{(dilution)}$ of 0.23 h^{-1} (Dillon et al., 2002; Sörgel et al., 2011a), a $[HONO]_{background}$ value of 10 pptv (Zhang et al., 2009), and taking the mean noontime [HONO] value of 400 pptv in this study, a value of about 0.09 ppbv h^{-1} can be derived, which is much smaller than L_{Phot} and can be ignored in the following discussion. The average daytime HONO emission rate from soil P_{soil} varied from 0.002 to 0.007

480   with a mean value of 0.004 ± 0.002 ppbv h^{-1}, which is three orders of magnitude smaller than L_{Phot}, and can also be ignored

in the following discussion. As a result, $P_{Unknown}$ can be expressed by Eq. (14), in which $\partial[HONO]/\partial t$ is substituted by $\Delta[HONO]/\Delta t$.

$$\frac{\Delta[HONO]}{\Delta t} = (P_{OH+NO} + P_{emis} + P_{Unknown}) - (L_{OH+HONO} + L_{Phot}) \tag{14}$$

485

Figure 6 shows the budget of HONO from 9:00 to 15:00. As expected, photolysis HONO L_{Phot} (1.58 ± 0.82 ppbv h^{-1}) was the main loss pathway in the day, followed by a small contribution by the homogeneous reaction of HONO + OH ($L_{OH+HONO}$, 0.07 ± 0.03 ppbv h^{-1}). Among the sources, P_{OH+NO} and $P_{Unknown}$ were comparable in magnitudes, with an average of 0.79 ± 0.61 ppbv h^{-1} and 0.65 ± 0.46 ppbv h^{-1}, respectively. $P_{Unknown}$ showed a photo-enhanced feature, reaching its maximum at
490   12:00 at 0.97 ppbv h^{-1}, similar to the observations in Xinken (Su et al., 2008b), Beijing (Yang et al., 2014), Wangdu (Liu et al., 2019a), Changzhou (Zheng et al., 2020) and Cyprus (Meusel et al., 2016). The average of $P_{Unknown}$ is comparable to the observation in Back Garden (0.77 ppbv h^{-1}) by Li et al. (2012), but smaller than those in Xinken ($\approx$ 2.0 ppbv h^{-1}) by Su et al. (2008b) and Guangzhou city area (1.25 ppbv h^{-1}) by Yang et al. (2017a). Homogeneous reaction of NO + OH reached its maximum in the early morning, and contributed the most fraction in the whole day. Apparently, high NO concentrations at
495   our site made P_{OH+NO} the biggest daytime source of HONO, exceeding $P_{Unknown}$, similar to observations at other high-NOx sites such as the Uintah Basin (Tsai et al., 2018), Houston (Wong et al., 2013), Denver (VandenBoer et al., 2013), Santiago de Chile (Elshorbany et al., 2009), London (Heard et al., 2004), Paris (Michoud et al., 2014), Beijing (Liu et al., 2021; Slater et al., 2020; Zhang et al., 2019; Liu et al., 2020b), Hebei (Xue et al., 2020) and Taiwan (Lin et al., 2006). Next, we investigate possible factors relating to $P_{Unknown}$.
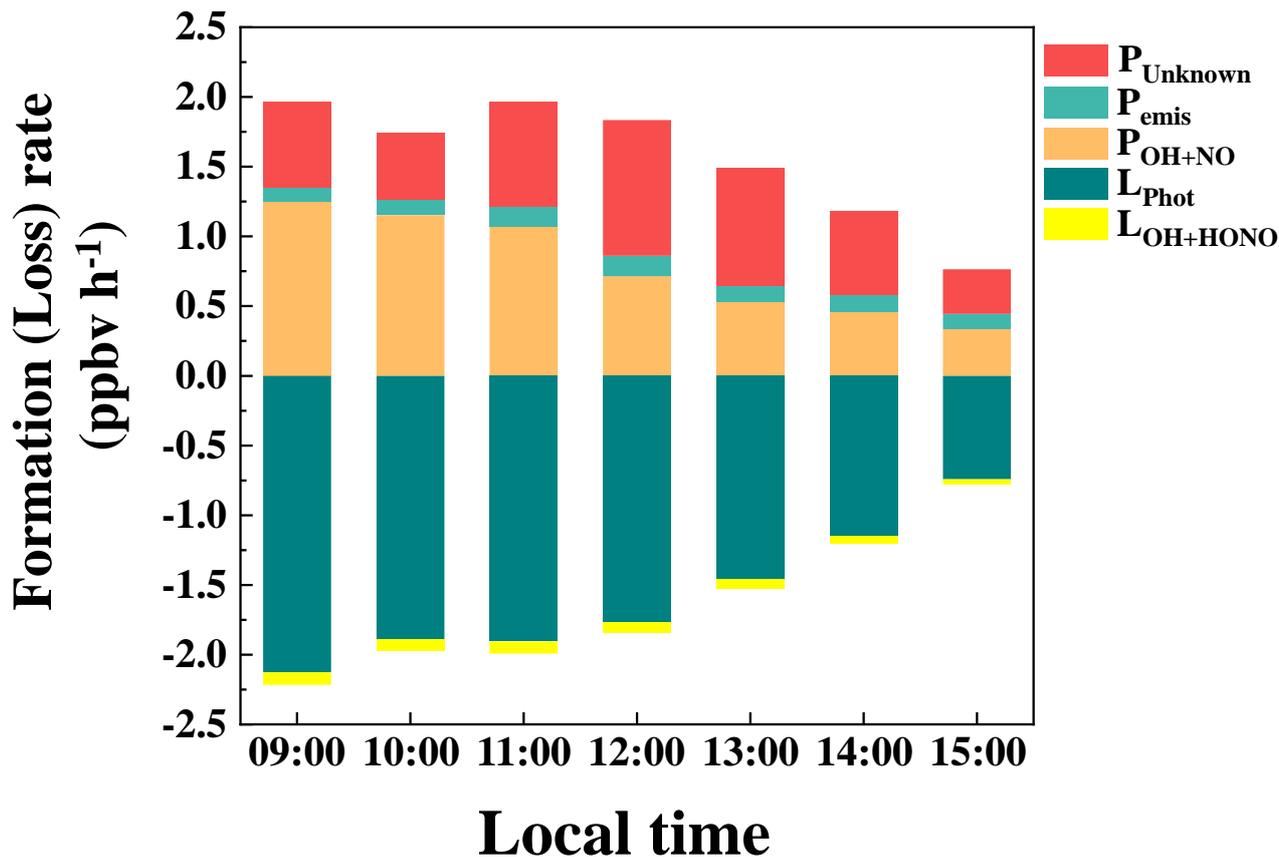
Figure 6. Items of the HONO budget (Eq. (14)) in Guangzhou during the observation period.

3.3.2 Possible mechanisms for daytime HONO production

Figure 7 shows that the correlation between $P_{Unknown}$ and NO_2 and $J(NO_2)$ was 0.0681 and 0.2713, respectively. The correlation between $P_{Unknown}$ and $NO_2 \times J(NO_2)$ further improved to 0.4116, indicating that $P_{Unknown}$ may be related to the photo-enhanced reaction of NO_2 (Jiang et al., 2020; Li et al., 2018a; Liu et al., 2019a; Liu et al., 2019b; Su et al., 2008b; Zheng et al., 2020; Huang et al., 2017). No correlation was found between $P_{Unknown}$ and $PM_{2.5}$ ($R^2 = 0.0001$), indicating that particulate matters may not be a key factor in daytime HONO production (Wong et al., 2012; Li et al., 2018a; Sörgel et al., 2011a; Wang et al., 2017a; Zheng et al., 2020). Meanwhile, the correlations between $P_{Unknown}$ and nitrate in PM_1 and the sum of gaseous nitric acid and nitrate in PM_1 were very low, with R^2 of 0.0348 and 0.0062 respectively. And the correlation between $P_{Unknown}$ and the product of nitrate and $J(NO_2)$ was also poor ($R^2 = 0.0073$), which does not relate $P_{Unknown}$ to the photolysis of nitrate or gaseous nitric acid. Wang et al. (2016) and Ge et al. (2019) suggested that NH_3 can efficiently

promote the reaction of NO_2 and SO_2 to form HONO and sulfate. However, we did not find good correlations for $P_{Unknown}$ vs. NH_3, $P_{Unknown}$ vs. SO_2, or $P_{Unknown}$ vs. $NH_3 \times SO_2$.

In summary, at our site with relatively strong traffic impact and high NO, NO + OH appears to be the largest daytime HONO source followed by an unknown photolytic source, which does not seem to be related to aerosols, nor does it seem to be related to the photolysis of nitrate/nitric acid, nor the reaction between NO_2, SO_2 and NH_3.
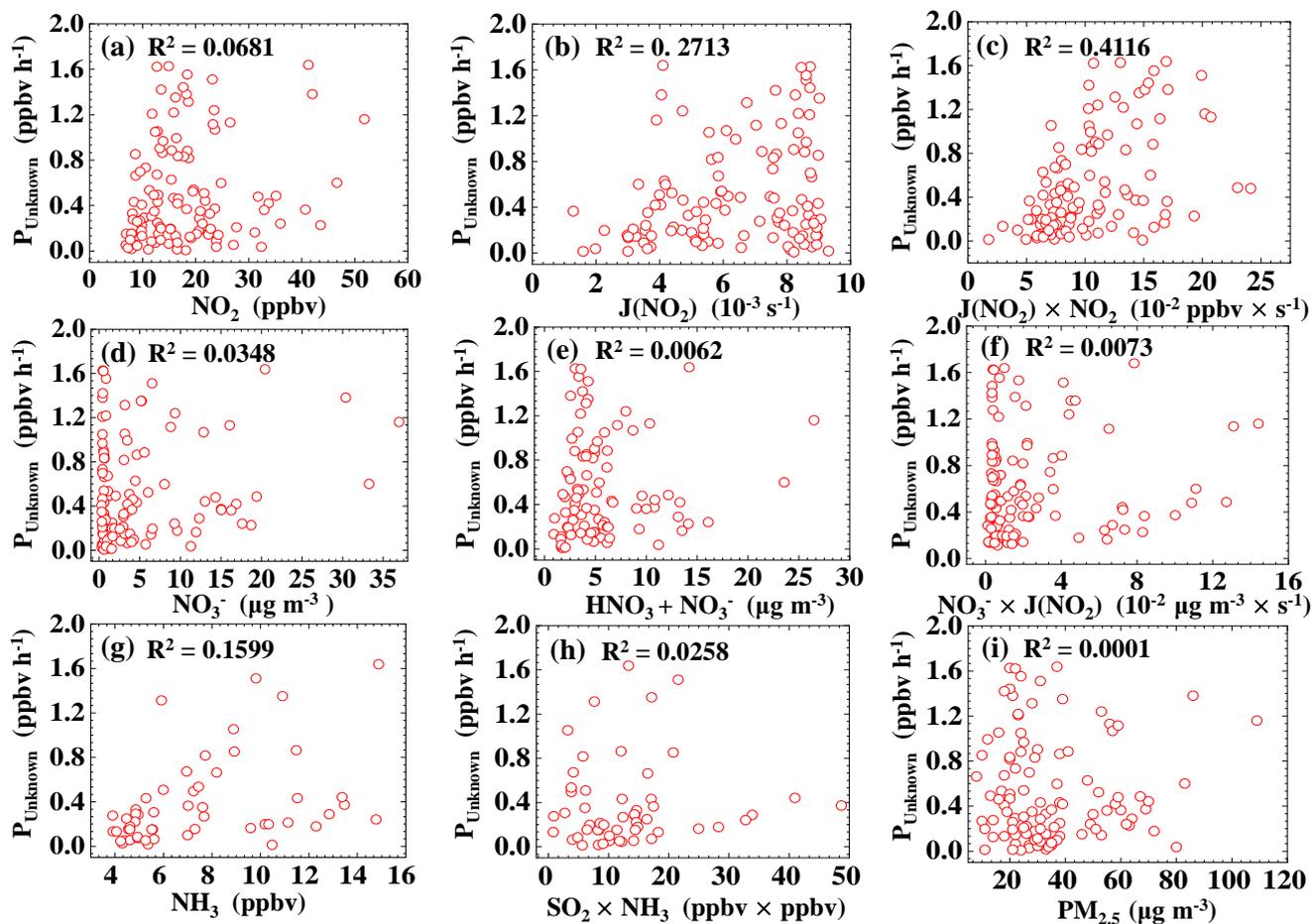
Figure 7. Correlations between daytime HONO unknown sources $P_{Unknown}$ and related parameters.

4 Conclusions

Nitrous acid (HONO) was measured with a custom-built LOPAP instrument, along with meteorological parameters and other atmospheric constituents at an urban site in Guangzhou in Pearl River Delta from 27 September to 9 November 2018. The HONO concentrations varied from 0.02 to 4.43 ppbv with an average of 0.74 ± 0.70 ppbv. Compared to prior

measurements in Guangzhou, a decreasing trend of HONO can be seen along with improved air quality in the city over the past decade.

We have investigated budget of HONO at this site using these data and our key findings are summarized as follows.

We found that the emission ratios (HONO/NOx) derived from an analysis of 11 fresh plumes varied from 0.1% to 1.5% with an average value of 0.9% ± 0.4%. Using this estimated emission ratio and an estimate of NOx emission rate extracted from a grid cell around our site in a high-resolution (3 km × 3 km) NOx emission inventory, we estimated a primary HONO emission rate of $0.30 ± 0.15$ ppbv h^{-1}, which turned out far larger (almost by an order of magnitude) than what would be estimated with a city-level NOx emission estimate, which does not adequately represent NOx emission rate specifically for the observation site. Thus, for future analysis of HONO data to properly estimate direct emission of HONO, we suggest that high quality emission data be used to reduce uncertainty. This is especially crucial for a site that receives nearby traffic emissions like ours.

HONO produced by the homogeneous reaction of NO + OH at night was $0.14 ± 0.30$ ppbv h^{-1}, which represents a secondary HONO source. Another major secondary HONO source at night is heterogeneous conversion of NO_2 on ground surface ($0.27 ± 0.13$ ppbv h^{-1}). Correlation analysis shows that the heterogeneous reaction of NO_2 related to NH_3 and RH may contribute to the nighttime HONO formation. These two secondary sources and the primary emission from vehicle exhaust (between $0.04 ± 0.02$ ppbv h^{-1} and $0.30 ± 0.15$ ppbv h^{-1} with a median value of $0.16 ± 0.07$ ppbv h^{-1}) were found to be the three largest sources of HONO at night. Because of the large range of those parameter values assumed in their calculations (e.g., the NO_2 uptake coefficient that spans two orders of magnitude), the relative importance of the three major sources depends on these assumptions. Soil emission ($0.019 ± 0.009$ ppbv h^{-1}) and heterogeneous NO_2 conversion on the aerosol surfaces ($0.03 ± 0.02$ ppbv h^{-1}) were two other minor sources. Our calculations suggested that dilution acted as a major sink ($0.18 ± 0.16$ ppbv h^{-1}), while loss of HONO on the aerosol surfaces played a much less important role. In order to balance the nighttime HONO budget and assuming dry deposition to be responsible for the remaining amount of HONO loss, a dry deposition rate of 2.5 cm s^{-1} is required, equivalent to a loss rate of $0.41 ± 0.31$ ppbv h^{-1}.

Daytime HONO budget analysis revealed that in order to sustain the observed HONO concentration around 450 pptv despite fast photolysis of HONO, an additional unknown source production rate ($P_{Unkonwn}$) of $0.65 ± 0.46$ ppbv h^{-1} was needed, in addition to primary emission P_{emis} at $0.12 ± 0.02$ ppbv h^{-1}, and the homogenous reaction source P_{OH+NO} at $0.79 ± 0.61$ ppbv h^{-1}. It is worth noting that the homogenous HONO source by NO + OH appeared to be a stronger source of HONO than the unknown source ($P_{Unkonwn}$), because of high levels of NO at our site. Correlation analysis between $P_{Unknown}$ and proxies of different mechanisms showed that $P_{Unknown}$ appeared to be photo-enhanced, and yet the mechanism remains unclear. Aerosols

did not appear to be as important as ground as a heterogenous reaction media, as suggested by the weak correlation between $P_{Unknown}$ and $PM_{2.5}$. No correlations were found between $P_{Unknown}$ and nitrate/HNO_3, NH_3 and SO_2.

560 Overall, these results from our study offer a unique perspective on HONO at an urban site receiving heavy traffic emissions in the PRD region. Our budget calculations and comprehensive uncertainty ananlysis suggest that at such locations as ours, HONO direct emissions and $NO + OH$ can become comparable or even surpass other HONO sources that typically receive greater attention and interest, such as the NO_2 heterogenous source and the unknown daytime photolytic source. Our findings emphasize the need to reduce the uncertainties of both conventional and novel HONO sources and sinks to advance our

565 understanding of this important source of atmospheric OH.

Data availability

The data used in this study are available from the corresponding author upon request (chengp@jnu.edu.cn).

Contribution

570 Peng Cheng organized the field campaign. Yihang Yu and Huirong Li analyzed the data and wrote the paper. All authors contributed to measurements, discussing results, and commenting on the paper. Yihang Yu and Peng Cheng contributed equally to this work.

Competing interests

The authors declare that they have no conflict of interest.

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