Budget of nitrous acid (HONO) and its impacts on atmospheric oxidation capacity at an urban site in the fall season of Guangzhou, China

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Abstract. Nitrous acid (HONO) can produce hydroxyl radicals (OH) by photolysis and plays an important role in atmospheric photochemistry. Over the years, high concentrations of HONO have been observed in the Pearl River Delta region (PRD) of China, which may be one reason for the elevated atmospheric oxidation capacity. A comprehensive atmospheric observation campaign was conducted at an urban site in Guangzhou from 27 September to 9 November 2018. During the period, HONO was measured from 0.02 to 4.43 ppbv with an average of 0.74 ± 0.70 ppbv. The emission ratios (HONO/NOx) of 0.9 ± 0.4% were derived from 11 fresh plumes. The primary emission rates of HONO at night were calculated to be between 0.04 ± 0.02 ppbv h^{-1} and 0.30 ± 0.15 ppbv h^{-1} based on a high-resolution emission inventory. The HONO formation rate by the homogeneous reaction of OH + NO at night was 0.26 ± 0.08 ppbv h^{-1}, which can be seen as secondary results from primary emission. They were both much higher than the increase rate of HONO (0.02 ppbv h^{-1}) during night. The soil emission rate of HONO at night was calculated to be 0.019 ± 0.001 ppbv h^{-1}. Assuming dry deposition as the dominant removal process of HONO at night, a deposition velocity of at least ~ 1.8 cm s^{-1} is required to balance the direct emissions and OH + NO reaction. Correlation analysis shows that NH_3 and relative humidity (RH) may participate in the heterogeneous transformation from NO_2 to HONO at night. In the daytime, the average primary emission P_{emis} was 0.12 ± 0.01 ppbv h^{-1}, and the homogeneous reaction P_{OH+NO} was 0.79 ± 0.61 ppbv h^{-1}, larger than the unknown sources $P_{Unknown}$ (0.65 ± 0.46 ppbv h^{-1}). These results suggest primary emissions as a key factor affecting HONO at our site, both during daytime and nighttime. Similar to previous studies, the daytime unknown source of HONO, $P_{Unknown,}$ appeared to be related

to the photo-enhanced conversion of NO_2. The daytime average OH production rates by photolysis of HONO was 3.7×10^6 cm^{-3} s^{-1}, lower than that from $O^1D + H_2O$ at 4.9×10^6 cm^{-3} s^{-1}. Simulations of OH and O_3 with the Master Chemical Mechanism (MCM) box model suggested strong enhancement effect of HONO on OH and O_3 by 59% and 68.8%, respectively, showing a remarkable contribution of HONO to the atmospheric oxidation in the fall season of Guangzhou.

Keywords: HONO; Atmospheric oxidation capacity; Budget analysis; Heterogeneous reaction

1 Introduction

As a primary source of hydroxyl radical (OH), HONO has attracted scientific researchers' great interest. The photolysis of HONO (Reaction R1) can generate a substantial amount of OH, which is a primary atmosphere oxidant that is responsible for oxidizing and removing of most natural and anthropogenic trace gases. Additionally, OH radicals can initiate the oxidation of the volatile organic compounds (VOC) to produce hydroperoxyl radicals (HO_2) and organic peroxy radicals (RO_2). These free radicals can further lead to the formation of ozone (O_3) in the presence of nitrogen oxides (NOx) (Xue et al., 2016; Finlayson-Pitts and Pitts, 2000; Hofzumahaus et al., 2009; Lelieveld et al., 2016; Tan et al., 2018). Up to 33–92% OH formation can be attributed to HONO photolysis in both rural and urban sites (Kleffmann et al., 2005; Michoud et al., 2012; Tan et al., 2017; Xue et al., 2020; Hendrick et al., 2014). However, the detailed formation mechanisms of HONO are still not well understood and the observed HONO concentrations cannot be completely explained by current research (Sörgel et al., 2011a; Kleffmann et al., 2005; Sarwar et al., 2008; Liu et al., 2019a; Lee et al., 2016; Liu et al., 2020c).

$$HONO + h\nu \rightarrow OH + NO \ (300\ nm < \lambda < 405\ nm) \quad (R1)$$

HONO sources generally include direct emissions, homogeneous reactions and heterogeneous reactions. HONO can be directly emitted into the troposphere from combustion processes such as biomass burning, vehicle exhaust, domestic heating, and industrial exhaust (Liu et al., 2019b; Neuman et al., 2016; Nie et al., 2015; Kramer et al., 2020). The emission ratios of HONO/NOx of traffic sources have been estimated in the range of 0.3%–0.85% through tunnel experiments considering various engine types (Kirchstetter et al., 1996; Kurtenbach et al., 2001; Kramer et al., 2020). Soil nitrite formed through the processes of biological nitrification and denitrification, were proposed to be a prominent HONO source in the troposphere (Maljanen et al., 2013; Oswald et al., 2013; Wu et al., 2019; Su et al., 2011). Subsequently, biological soil crusts (biocrusts) were also found to release HONO (Weber et al., 2015; Porada et al., 2019; Meusel et al., 2018). In addition, an acid displacement mechanism has also been suggested to contribute substantial fraction of daytime HONO formation (VandenBoer et al., 2015). The reaction between NO and OH is considered an important pathway of HONO formation when OH and NO concentrations are relatively high (Alicke et al., 2002; Li et al., 2012; Pagsberg et al., 1997; Qin et al., 2009; Wong et al., 2011), whereas this pathway often cannot explain the observed HONO concentrations, especially during

daytime (Tang et al., 2015; Li et al., 2010; Czader et al., 2012; Tong et al., 2016). Bejan et al. (2006) studied the HONO formation by the photolysis of different gaseous nitrophenols and proposed that the photolysis of nitrophenols can partly explain the observed HONO formation in the urban atmosphere. Zhang and Tao (2010) proposed that HONO can form through homogeneous nucleation of NH_3, NO_2 and H_2O. However, this reaction has not yet been observed in field experiments nor tested by laboratory studies. Li et al. (2014b) proposed that the reaction of NO_2 with $HO_2{\cdot}H_2O$ could be a gas-phase source of HONO in the lower troposphere. But Ye et al. (2015) estimated the HONO yield of the reaction of NO_2 with $HO_2{\cdot}H_2O$ was only 3%. Additionally, heterogeneous reactions on different kinds of surfaces have also been found to be possible significant HONO sources, including heterogeneous reactions of NO_2 on ground surfaces (Meusel et al., 2016; VandenBoer et al., 2013), building surfaces (Acker et al., 2006; Indarto, 2012), ocean surfaces (Wen et al., 2019; Wojtal et al., 2011; Yang et al., 2021a), soil surfaces (Laufs et al., 2017; Kleffmann et al., 2003; Yang et al., 2021b) and vegetation surfaces (Stutz et al., 2002; Marion et al., 2021), etc. Photosensitized reduction reaction of NO_2 on organic surfaces (such as humic acids and aromatics) has been considered as an effective pathway to generate HONO (George et al., 2005; Stemmler et al., 2006; Liu et al., 2020a; Ammar et al., 2010; Brigante et al., 2008; Cazoir et al., 2014; Sosedova et al., 2011). The heterogeneous conversion of NO_2 to HONO on humid surfaces have also been studied (Finlayson-Pitts et al., 2003; Ammann et al., 1998; Ndour et al., 2008) and this conversion can be further promoted by ambient NH_3 and SO_2 (Ge et al., 2019; Wang et al., 2016; Xu et al., 2019; Li et al., 2018b; Wang et al., 2021). In addition, HONO can also be formed by heterogeneous conversion of NO_2 on secondary organic aerosols and fresh soot particles (Arens et al., 2001; Ziemba et al., 2010), but the contributions and mechanisms are still under discussion (Arens et al., 2001; Aubin and Abbatt, 2007; Bröske et al., 2003; Qin et al., 2009). Both field observations and laboratory studies found that the photolysis of adsorbed HNO_3 and particulate nitrate (NO_3^-) made an important contribution to HONO formation (Ye et al., 2016; Ye et al., 2017; Zhou et al., 2003; Zhou et al., 2002b; Zhou et al., 2011; Ziemba et al., 2010). However, Laufs and Kleffmann (2016) obtained a very low HNO_3 photolysis frequency in laboratory, almost two orders of magnitude lower than the result by Zhou et al. (2003).

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 deterioration of air quality in this region, which was characterized by atmospheric "compound pollution" with concurrent 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). While O_3 has been increasing along with reduced $PM_{2.5}$ over recent years in the region (Li et al., 2014a; Liao et al., 2020; Wang et 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. By far two comprehensive atmospheric observations were conducted in the PRD region to detect OH radicals. High concentrations of OH radicals were observed both times, especially in the first time it was the highest ever-reported, which cannot be explained by the current knowledge of atmospheric chemistry (Hofzumahaus et al., 2009). Substantial level of HONO was suggested to be the major source of the OH–HO_2–RO_2 radical system in above two campaigns (Lu et al., 2012; Tan et al.,

2019a). Moreover, high concentrations of HONO have also been confirmed in other observations in this area during last two decades (Hu et al., 2002; Su et al., 2008b; Su et al., 2008a; Qin et al., 2009; Li et al., 2012; Shao et al., 2004). Fast OH production through HONO photolysis may be a key factor for the increasing atmospheric oxidation capacity and ozone concentration in this area.

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 campaign named "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 years. 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. By analysing our observational data, both nighttime HONO formation pathways and daytime HONO budgets have been investigated in this study. The contribution of HONO photolysis to OH production has been calculated and compared with that of O_3 photolysis and ozonolysis of alkenes. The impact of HONO on atmospheric oxidation capacity and O_3 formation is further investigated using a chemical box model based on Master Chemical Mechanism (MCMv3.3.1).

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, ambient VOCs were measured using a TH-300B On-Line VOCs Monitoring System involving detection technology of ultralow temperature preconcentration coupled with gas chromatography-mass spectrometry (GC/MS) with the time resolution of 1 h. NOx (NO + NO_2) was measured by a nitrogen oxides analyzer (Thermo Scientific, Model 42i), which used a NO-NO_x chemiluminescence detector equipped with a molybdenum-based converter with the time resolution and detection limit of 1 min and 1 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%, 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 1 ppbv respectively. CO was measured by a CO analyzer (Thermo Scientific, Model 48i) with the time resolution and detection limit of 1 min and 0.1 ppmv respectively. NH_3 was measured by laser absorption spectroscopy (PICARRO, G2508) with the time resolution and detection limit of 1 min and 1 ppbv respectively. 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 Accelerator 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), J(H_2O_2) and J(O^1D) were measured by a filter radiometry (Focused Photonics Inc., PFS-100) with a time resolution of 1 min.

2.3 Box model

To evaluate the influence of HONO chemistry on the atmospheric oxidation capacity, a zero dimensional box model (Framework for 0-Dimensional Atmospheric Modeling–F0AM) based on the Master Chemical Mechanism (MCMv3.3.1) (Wolfe et al., 2016; Jenkin et al., 2003; Jenkin et al., 2015) was applied to calculate the concentrations of O_3 and OH radicals. The Master Chemical Mechanism describes atmospheric gas-phase organic chemistry in detail which has been widely used in atmospheric chemistry modelling. Kinetic rate coefficients were derived from the MCM v3.3.1 website (http://mcm.leeds.ac.uk/MCM). The model was implemented in MATLAB 2012. In this work, the boundary layer diurnal cycle has been modified and the dilution factor k_{dil} was set at 86400^{-1} s. The solar zenith angle was calculated based on

longitude, latitude and time of the observation. Photolysis rate correction coefficient j_{corr} was set to 1. The model simulation was constrained by hourly averaged measurement data, including HONO, NO, NO_2, CO, SO_2, VOC species (listed in Table S2), and temperature, water vapor, wind speed, wind direction, pressure and photolysis frequencies $J(NO_2)$, J(HONO), $J(O^1D)$ and $J(H_2O_2)$. Other non-measured photolysis frequencies were calculated according to Eq. (1) (Jenkin et al., 1997), and then scaled by the measured $J(NO_2)$:

$$J_i = L_i \cos(\chi)^{M_i} \exp(-N_i \sec(\chi)) \quad (1)$$

where χ represents the solar zenith angle (SZA); L_i, M_i and N_i are the photolysis parameters under clear sky conditions which were taken from Jenkin et al. (1997). The heterogeneous processes as well as deposition of chemical species were not considered in this model. The simulation results were evaluated by comparing against the measurements, and index of agreement (IOA), a statistical parameter was employed for the evaluation (Jeon et al., 2018; Xing et al., 2019; Li et al., 2010). Two simulations with and without HONO constrained by measured values were conducted to examine the impact of HONO on OH and O_3 formation.

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.

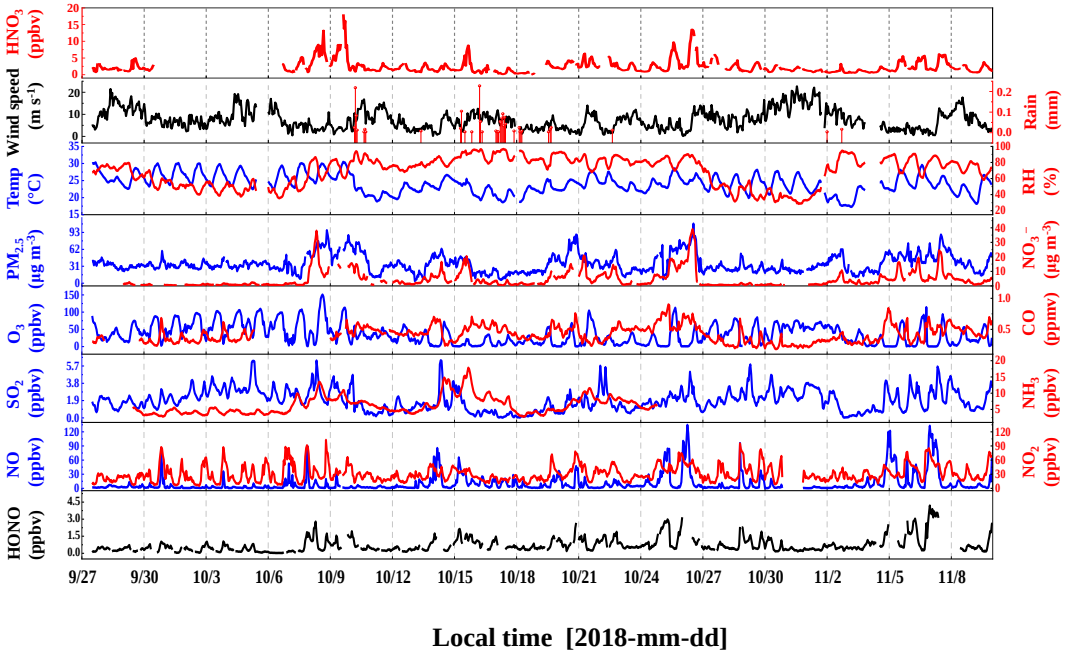

Figure 1. Temporal variations of meteorological and pollutants during the observation period.

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.

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Location	Date	HONO (ppbv)	HONO (ppbv)		NO_2 (ppbv)		NOx (ppbv)		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*
This work	*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

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^1D) and J(NO_2) in the whole observation period are shown in Fig. S3. The maximum values of J(HONO), J(O^1D) 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 in cities and rural sites (Lee et al., 2016; Xue et al., 2020; Villena et al., 2011; Yang et al., 2021c). 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 indicates 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 0.2% to 9.1% with an average of 2.3 ± 1.3%, which is lower than most previous field observations in PRD region (Li et al., 2012; Qin et al., 2009; Xu et al., 2015), and is typical for relatively fresh plumes. Previous many field observations also reported low values of HONO/NO_2 ranging from 2% to 10% in freshly polluted air masses (Febo et al., 1996; Lammel and Cape, 1996; Sörgel et al., 2011b; Stutz et al., 2004; Zhou et al., 2007; Su et al., 2008a). The relatively stable and low value of HONO/NO_2 in nighttime seems to indicate the low contribution of heterogeneous reactions of NO_2 to HONO concentrations.

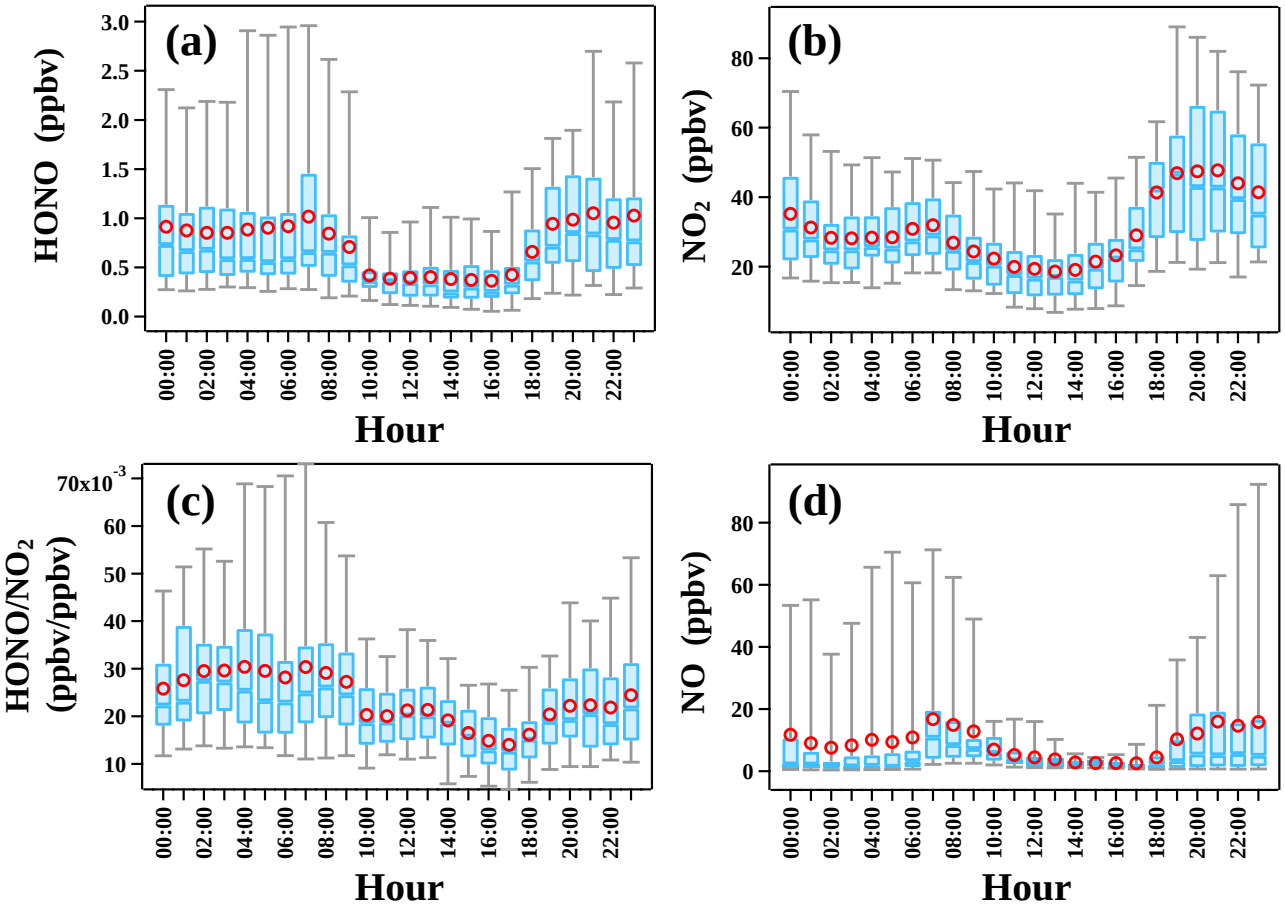


Figure 2. Diurnal profiles of HONO, NO_2, NO and HONO/NO_2 during the observation period. The blue line in the box and red circle refer to the median and mean, respectively. Boxes represent 25% to 75% of the data, and whiskers 95% of the data. The box plots presented in this study is generated by an Igor Pro-based computer program, Histbox (Wu et al., 2018).

3.2 Nocturnal HONO formation and sources

3.2.1 Direct emissions

As noted in Sect. 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 criteria (a)–(e) (see Table S3). 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% measured in Hong Kong (Xu et al., 2015), 1.0% observed in Hong Kong (Yun et al., 2017), 0.79% measured in Nanjing (Liu et al., 2019b) and 0.69% observed in Changzhou (Shi et al., 2020b). It should be noted that the emission factor derived in this study is based on field observation and the screening criterion for fresh air mass is 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 evaluate the primary emission, three methods have been used in previous studies (Liu et al., 2019b; Liu et al., 2020b; Meng et al., 2020). In method (1), $[HONO_{emis}]$ (the primary emission's contribution to HONO concentration) is equal to the product of emission coefficient K and observed NOx concentration (Cui et al., 2018; Huang et al., 2017) (see Eq. (2)). This method ignores the sink of NOx and HONO, as well as transport and convection. On this basis, the observed NOx is equal to the accumulation of NOx emission, and HONO emission is linearly related to NOx concentration. However, ubiquitous loss of NOx would increase the uncertainty of this method, especially during daytime. In method (2), primary emission rate P_{emis} is equal to the product of emission coefficient K and $[\Delta NOx]$, the increase of NOx concentration during Δt (Liu et al., 2019b; Zheng et al., 2020) (see Eq. (3)). The promise of this method is similar to method (1), and it can only be used when NOx is increasing. As expected, a decrease in NOx would yield a negative HONO emission rate, which is unrealistic. In method (3), 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. (4)). 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 that emission inventory data with high spatial and temporal resolution are used to obtain an accurate estimate.

$$[HONO_{emis}] = K \times [NOx] \quad (2)$$

$$P_{emis} = K \times [\Delta NOx] \quad (3)$$

$$P_{emis} = K \times NOx^* \quad (4)$$

$$P_{HONO} = \frac{[HONO]_{t2} - [HONO]_{t1}}{t_2 - t_1} \quad (5)$$

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 by Fan et al. (2008).

The observed HONO production/accumulation rate P_{HONO} is calculated by Eq. (5), where $[HONO]_{t1}$ and $[HONO]_{t2}$ represent the HONO concentration at 18:00 and 6:00 Local Time, respectively. Then an average P_{HONO} of 0.02 ppbv h^{-1} can be derived. Hourly HONO primary emission rates calculated with the two inventories are shown in Fig. 3. 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}). The average of P_{emis} is 0.30 ± 0.15 ppbv h^{-1}, far larger than the average accumulating rate of HONO at night (0.02 ppbv h^{-1}) derived from observed HONO variation. 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., 2020b; Liu et al., 2020c) and a suburban site (Michoud et al., 2014), while the result at a rural site is much lower (Su et al., 2008b). The lower limit of the calculated P_{emis} is still larger than the observed HONO accumulation rate. Considering the uncertainty of the inventories (-25%–28%), P_{emis} may be overestimated or underestimated to the same extent. Nevertheless, direct emission of HONO is still a large HONO source at night along with other sources of HONO that remain to be considered. Furthermore, a large sink of HONO was necessary to explain the observed trend of HONO.

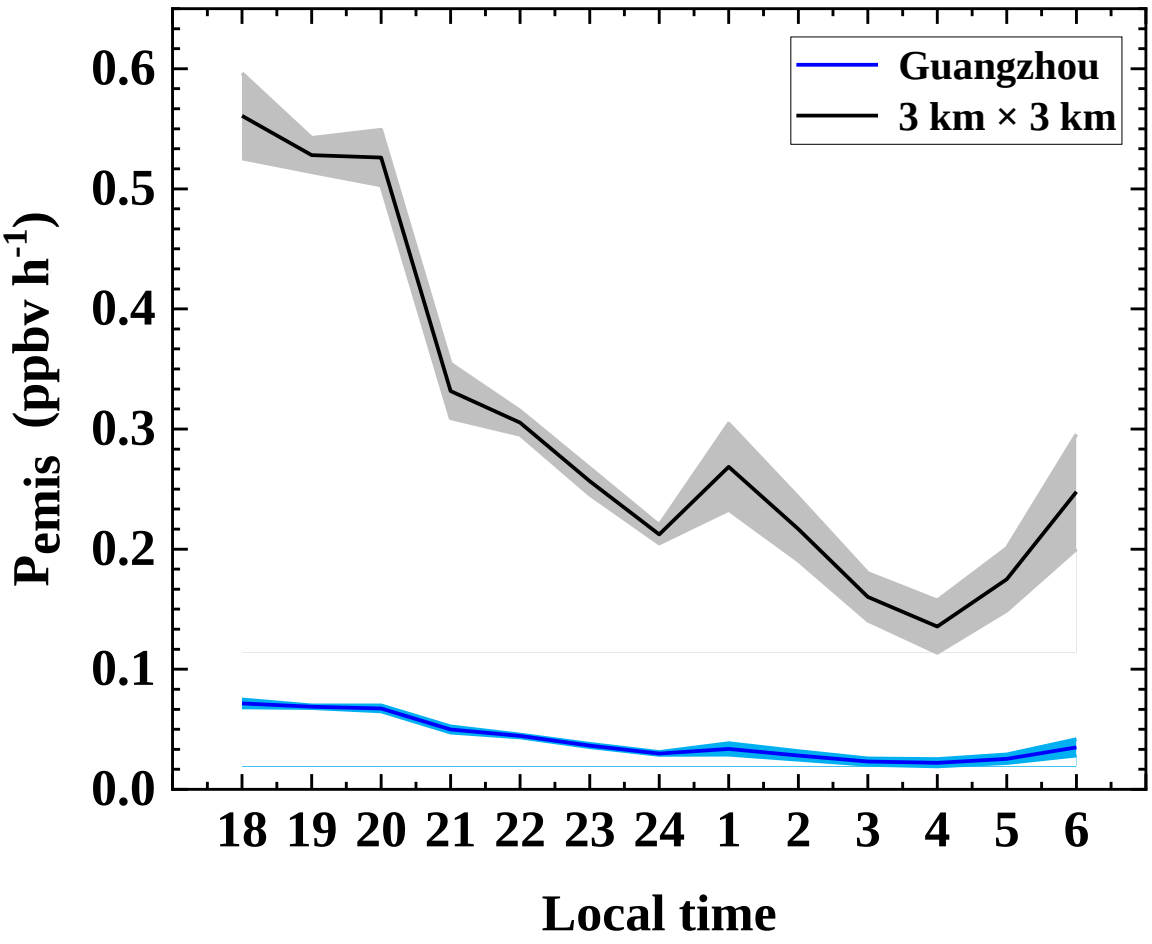


Figure 3. The nocturnal variation of HONO primary emission rates. The black and blue lines represent the HONO primary emission rates calculated by the 2017 NOx emission source inventory of the 3 km × 3 km grid cell centred on the Guangzhou Institute of Geochemistry and the 2017 NOx emission source inventory of Guangzhou city respectively. The coloured areas represent 1 – σ standard deviations.

Method (1) is also adopted here to calculate $[HONO]_{emis}$, and $[HONO]_{emis}/[HONO]$ can simply represent the primary emission's contribution to HONO. We summarized $[HONO]_{emis}/[HONO]$ ratios obtained from urban sites in China (Table S4). The values varied at a wide range from 12% to 52%, and the difference of 2 times or more existed in different seasons at the same site. These indicate the complexity of the impact of source emissions on observation site. The ratio of $[HONO]_{emis}/[HONO]$ at our site is at a high level of 47%, indicating that the site during the campaign is more strongly affected by primary emission from vehicle exhaust compared to most previous studies.

In addition to traffic emissions, we also estimated the HONO emission rate from soil P_{soil} (ppbv h^{-1}) according to Eq. (6):

$$P_{soil} = \frac{\alpha F_{soil}}{H} \quad (6)$$

where F_{soil} is the emission flux (g m^{-2} s^{-1}); H is the height of boundary layer (H, 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 ± 0.001 ppbv h^{-1}. It is comparable to the lower limit of primary emission rate of 0.04 ± 0.02 ppbv h^{-1}.

3.2.2 NO + OH homogeneous reaction

The reaction between NO and OH acts as the principle 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). Taking the homogeneous Reactions R2 and R3 into account, the net HONO homogeneous production rate can be calculated by following Eq. (7):

$$NO + OH \rightarrow HONO \quad (R2)$$

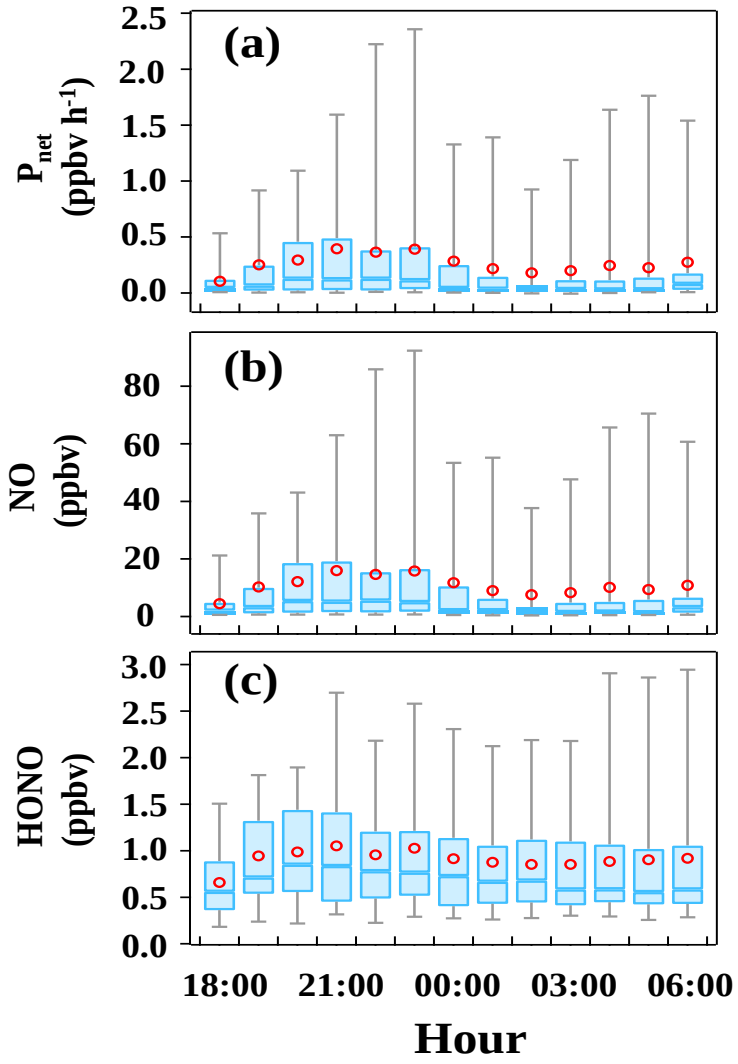
$$HONO + OH \rightarrow NO_2 + H_2O \quad (R3)$$

$$P_{net} = k_{NO+OH}[NO][OH] - k_{HONO+OH}[HONO][OH] \quad (7)$$

In Eq. (7), 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 R2 and R3 at 298 K, respectively (Li et al., 2012). Since the OH concentration was not measured, an average nighttime value of 1.0×10^6 cm^{-3} measured in Heshan in the PRD region in autumn of 2014 was assumed (Liu, 2017). As shown in Fig. 4, the variation of P_{net} is highly similar to NO, for the concentration of NO was 10 times larger than HONO. And the average value of P_{net} is 0.26 ± 0.08 ppbv h^{-1}, leading to a cumulative HONO contribution of 3.24 ppbv. However, the measured HONO only increased 0.26 ppbv in this period. It suggests that, (1) the reaction between NO and OH is adequate to explain the HONO increase in the whole night, even though other sources like NO_2 heterogeneous conversion might still exist; (2) except for HONO + OH, the strength of HONO sink should be at least 0.30 ppbv h^{-1}, 6 times larger than that obtained by Li et al. (2012) and comparable to that by Hao et al. (2020).

We carried out sensitivity tests using one tenth, twice and half of assumed OH concentration (1.0×10^6 cm^{-3}) (Lou et al., 2010). As is shown in Table S5, within the range of nighttime OH concentration, the cumulative production of the

homogeneous reaction of NO + OH in this study are all larger than the averaged measured accumulation of HONO, indicating that taking a value within the range of the observed nighttime OH concentration will not affect the conclusion of this study.



335 **Figure 4. The mean nocturnal variation of P_{net}, HONO and NO. The blue line in the box and red circle refer to the median and mean, respectively. Boxes represent 25% to 75% of the data, and whiskers 95 % of the data.**

3.2.3 NO_2 to HONO heterogeneous conversion

Our analysis so far suggests that direct emissions and the homogeneous reaction between NO and OH are more than sufficient to explain the growth of HONO concentration through the night. The relatively high correlation (R^2 = 0.5927)

between HONO and NO is in line with this finding (Fig. 5 (a)). In addition, correlation analysis was conducted to explore possible pathways of heterogeneous NO_2 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 5 (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 (Zhang et al., 2016), 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; Zhang and Tao, 2010; Wang et al., 2021).

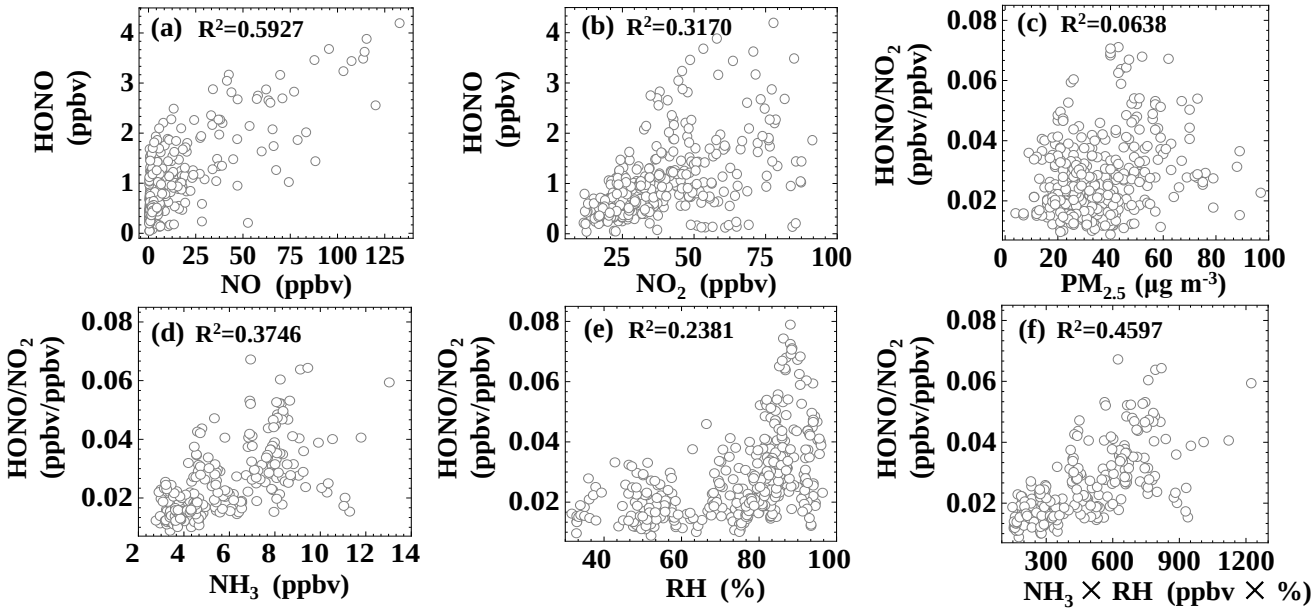


Figure 5. Correlations between HONO, $HONO/NO_2$ and various parameters during the time interval of 18:00–6:00.

In Fig. 6, 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_2O. 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., 2019b), 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 to vary across locales, likely reflecting the different composition of the ground surfaces, e.g., 60% for Chengdu (Yang et al., 2021c), 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).

In sum, our correlation analysis for $HONO/NO_2$ suggests that nighttime heterogenous conversion of NO_2 into HONO at our site might be related to NH_3 and water vapor, whereas aerosol surfaces appeared unimportant.

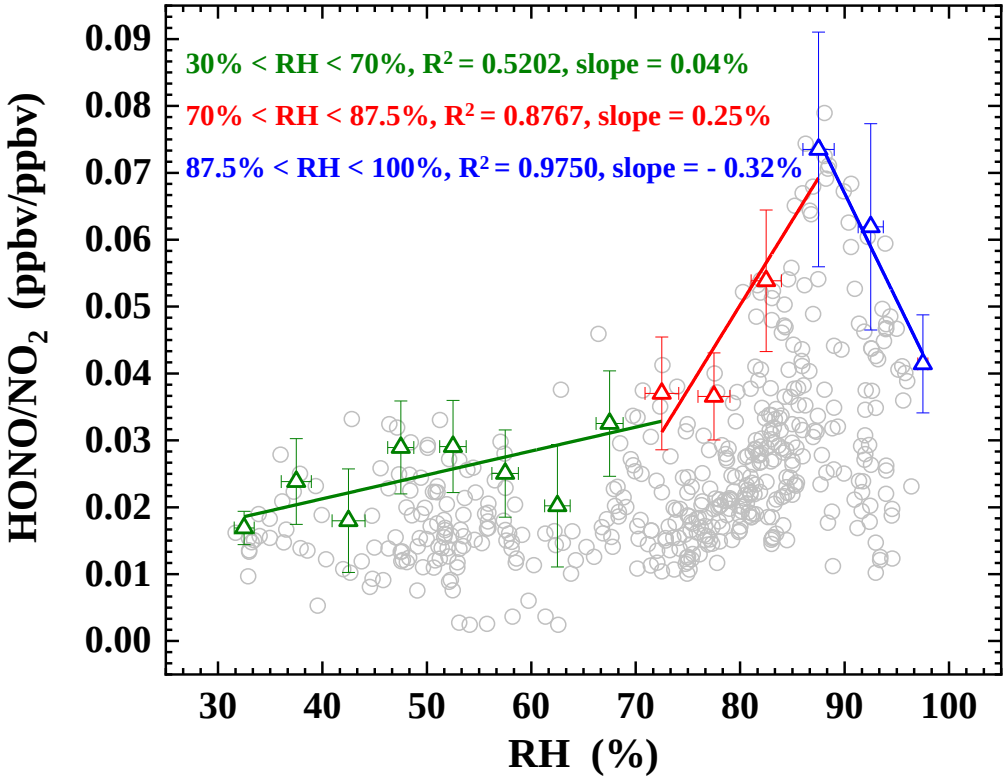


Figure 6. Scatter plot of $HONO/NO_2$ ratio against RH during nighttime from 18:00 to 6:00. Triangles are the average of top-5 $HONO/NO_2$ values in each 5% RH interval.

3.2.4 Removal of HONO through dry deposition

As discussed in Sect. 3.2.2, a sink of at least 0.30 ppbv h^{-1} is 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 HONO is mainly removed through deposition on the ground. HONO dry deposition velocity V_d can be estimated with Eq. (8):

$$\frac{d[HONO]}{dt} = P_{emis} + P_{soil} + P_{net} - \frac{V_d \times [HONO]}{H} \quad (8)$$

The average deposition velocity V_d between 18:00–6:00 was calculated to be 1.8 cm s^{-1}, which is within the range of prior researches (0.077–3 cm s^{-1}) (Harrison and Kitto, 1994; Harrison et al., 1996; Stutz et al., 2002; Li et al., 2012; Spindler et al., 1999), and also consistent to the results derived from the HONO uptake coefficient on soil and ground (Donaldson et al., 2014; VandenBoer et al., 2013). It should be noted that heterogeneous conversion of NO_2-HONO has not been taken into account, so 1.8 cm s^{-1} is the lower limit of dry deposition velocity. High RH at night probably increased the amount of adsorbed water on the ground surfaces and facilitates dry deposition of HONO.

In sum, primary emission from vehicle exhaust (between 0.04 ± 0.02 ppbv h^{-1} and 0.30 ± 0.15 ppbv h^{-1}) and the homogeneous reaction of OH + NO (0.26 ± 0.08 ppbv h^{-1}) were major sources of HONO at night. Nighttime soil emission rate was calculated to be 0.019 ± 0.001 ppbv h^{-1}, which is comparable to the observed nocturnal increase rate of HONO (0.02 ppbv h^{-1}), further indicating the importance of direct emissions. Additionally, contribution from NO_2 heterogeneous reactions on surfaces should not be ruled out. To balance the nighttime HONO budget by assuming dry deposition to be the principal loss process, a dry deposition rate of at least 1.8 cm s^{-1} is required.

3.3 Daytime HONO budget and unknown sources analysis

In this section, we concentrate on the daytime chemistry of HONO by a detailed budget analysis. The time variation of HONO concentration at our site can be related to its sources and sinks as follows:

$$\frac{\partial[HONO]}{\partial t} = P_{HONO} - L_{HONO} = (P_{OH+NO} + P_{Unknown} + P_{emis} + P_{soil} + T_V + T_H) - (L_{OH+HONO} + L_{Phot} + L_{Dep}) \quad (9)$$

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 R3, 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

with L_{Phot} = J(HONO) × [HONO]; L_{Dep} represents the deposition loss rate of HONO and can be calculated as $L_{Dep} = V_d \times [HONO]/H$, where V_d is the deposition velocity of HONO and H is the daytime mixing height. Assuming a daytime V_d of 1.6 cm s^{-1} (Hou et al., 2016; Li et al., 2011) and an 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.

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 peak values of $1.5–2.6\times10^7$ 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 of primary emission on HONO.

To minimize interferences, we choose 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 (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 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 with a mean value of 0.004 ± 0.001 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. (10), in which $\partial[HONO]/\partial t$ is substituted by $\Delta[HONO]/\Delta t$.

$$\frac{\Delta[HONO]}{\Delta t} = (P_{OH+NO} + P_{emis} + P_{Unknown}) - (L_{OH+HONO} + L_{Phot}) \quad (10)$$

Figure 7 shows the budget of HONO from 9:00 to 15:00. As expected, photolysis HONO L_{Phot} (1.58 ± 0.82 ppbv h^{-1}) is 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 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 (≈ 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 our site made P_{OH+NO} the biggest daytime source of HONO, exceeding $P_{Unknown}$, similar to other high-NOx sites such as 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., 2019b; Liu et al., 2020c), Taiwan (Lin et al., 2006) and Hebei (Xue et al., 2020). Next, we investigate possible factors relating to $P_{Unknown}$.

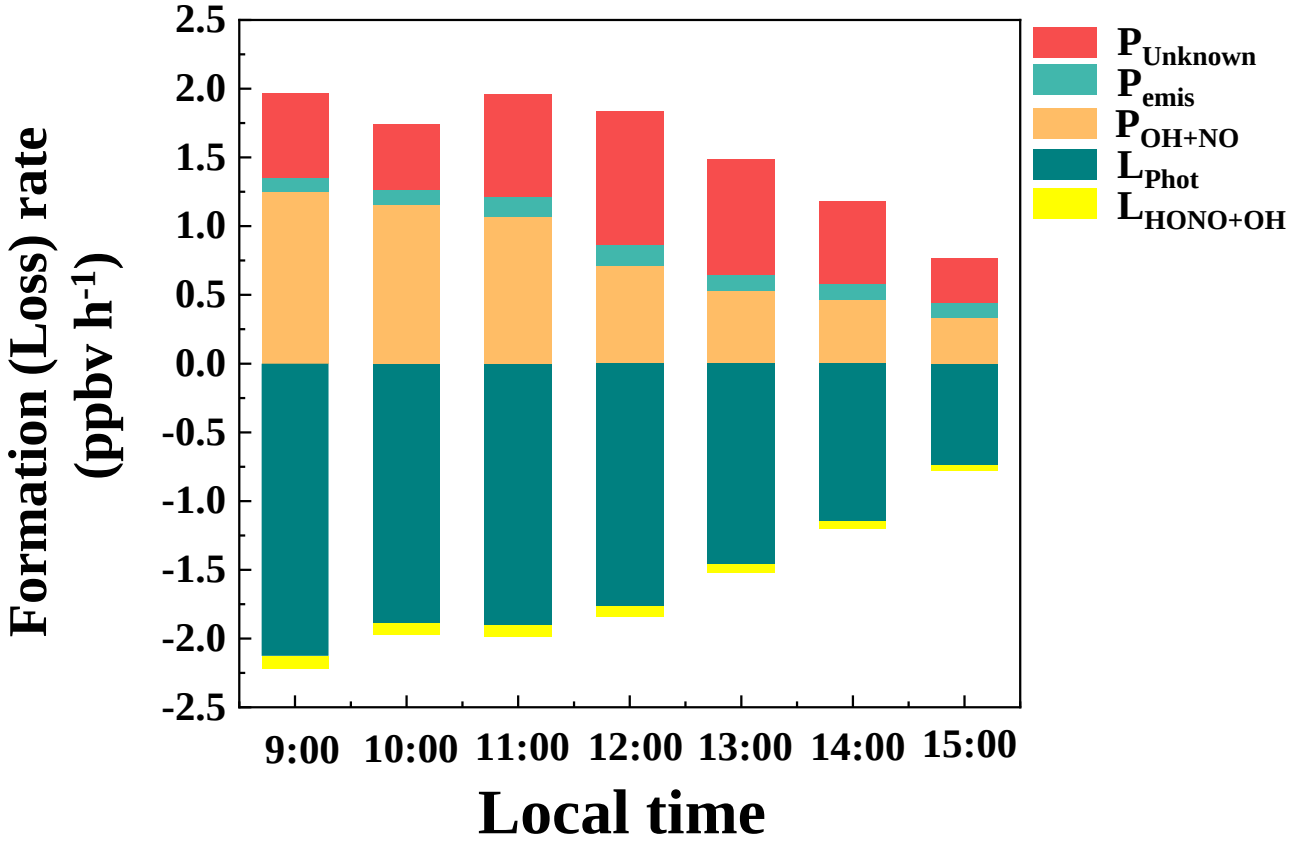


Figure 7. Items of the HONO budget (Eq. (10)) in Guangzhou during the observation period.

Figure 8 shows 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 × $J(NO_2)$ 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 = 0.00014), 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 = 0.0007, 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 the photolysis of nitrate/nitric acid, nor the reaction between NO_2, SO_2 and NH_3.

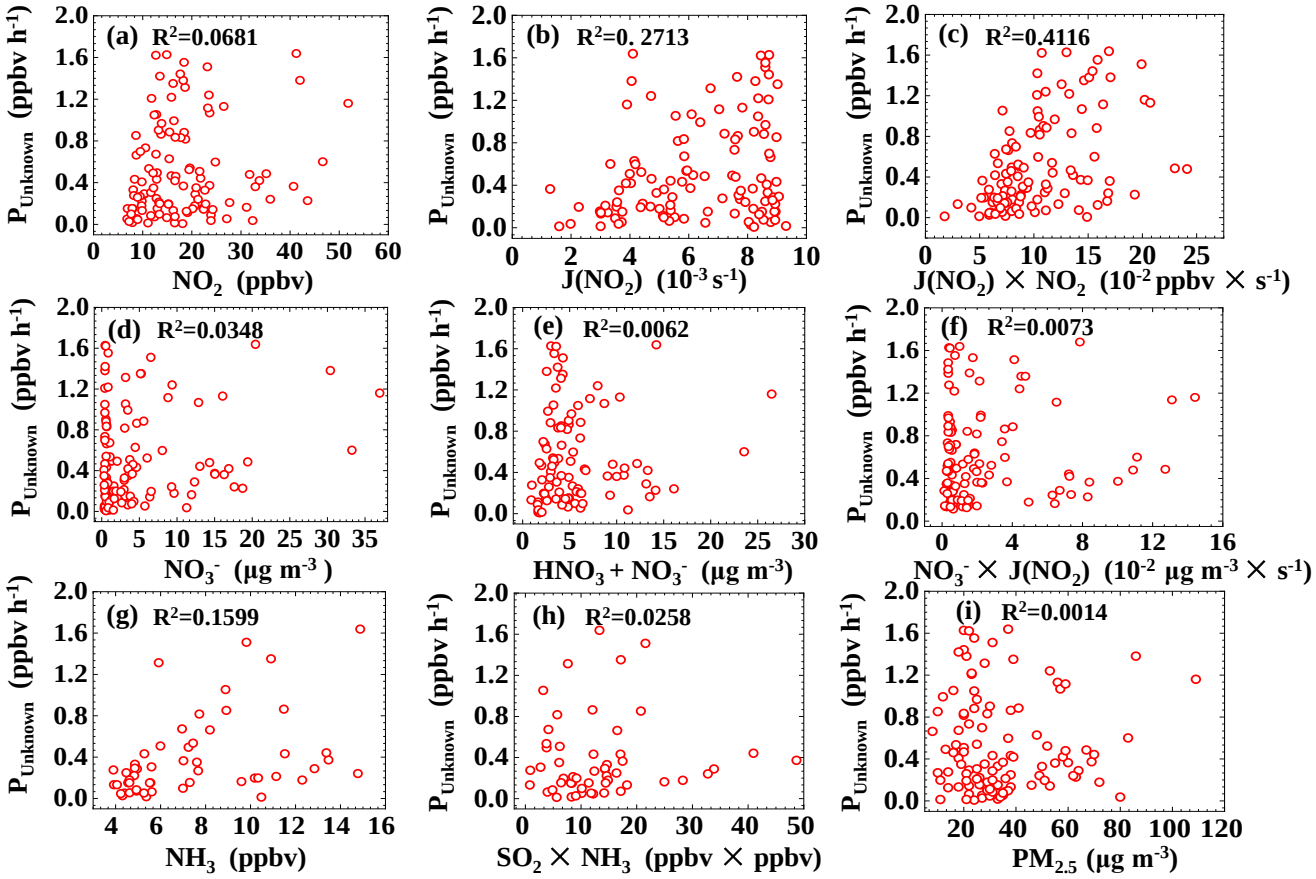


Figure 8. Correlations between daytime HONO unknown sources $P_{Unknown}$ and related parameters.

3.4 The contribution of HONO, O_3 and ozonolysis of alkenes to OH

Photolysis of HONO and O_3 contribute dominant the primary source of OH radicals. Ozonolysis of alkenes was found to be important source of OH (Heard et al., 2004; Elshorbany et al., 2009; Tan et al., 2019b). Here we evaluated and compared the contribution of the three pathways. Other sources such as the photolysis of peroxides, is usually not very significant in urban areas, especially during daytime, thus was not considered in this study (Li et al., 2018a; Shi et al., 2020b). The contribution of HCHO photolysis to OH was also not considered due to the lack of measurement for HCHO. The OH radicals' production rate from HONO photolysis $P_{OH(HONO)}$ can be calculated from the measured photolysis frequencies and the mixing ratios of HONO using Eq. (11). The net OH radicals' production from HONO $P_{(HONO-OH)}$ can be calculated by subtracting the OH loss caused by Reactions R1 and R2 from $P_{OH(HONO)}$ (Eq. (12)). The OH radicals' production rate from O_3 photolysis $P_{(O_3-OH)}$ can be calculated from Eq. (13). Only part of $O(^1D)$ atoms, formed through the photolysis of O_3 at solar radiation below 320 nm (Reaction R4), can generate OH radicals by reacting with water vapor (Reaction R5) in the atmosphere, so we used the absolute mixing ratio of water vapor, which can be derived from the temperature and relative humidity data, to calculate the

fraction of OH (Φ_{OH}) between Reactions R5 and R6. The reaction rate of $O(^1D)$ with N_2 and O_2 is 3.1×10^{-11} cm^3 s^{-1} and 4.0×10^{-11} cm^3 s^{-1} respectively (Seinfeld and Pandis, 2016). In Eq. (15), $k_{alkenes(i)+O_3}$ represents the reaction rate constant for the reaction of O_3 with alkene (i), and Y_{OH_i} represents the yield of OH from the gas-phase reaction of O_3 and alkene (i). Table S6 summarized the reaction rate constant of O_3 with alkenes at 298 K and the yields of OH.

$$P_{OH(HONO)} = J(HONO)[HONO] \quad (11)$$

$$P_{(HONO-OH)} = P_{OH(HONO)} - k_{NO+OH}[NO][OH] - k_{HONO+OH}[HONO][OH] \quad (12)$$

$$P_{(O_3-OH)} = 2\Phi_{OH}[O_3]J(O^1D) \quad (13)$$

$$\Phi_{OH} = k_5[H_2O]/(k_5[H_2O]+k_6[M]) \quad (14)$$

$$P_{(O_3+alkenes)-OH} = \sum k_{alkenes(i)+O_3}[alkenes(i)][O_3]\, Y_{OH_i} \quad (15)$$

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \ (\lambda < 320 \text{ nm}) \quad (R4)$$

$$O(^1D) + H_2O \rightarrow 2OH \quad (R5)$$

$$O(^1D) + M \rightarrow O(^3P) + M \ (M \text{ is } N_2 \text{ or } O_2) \quad (R6)$$

Figure 9 shows that $P_{(HONO-OH)}$ was larger than $P_{(O_3-OH)}$ before 10:00, while the latter became always higher with the solar radiation enhanced after 10:00. Both the two sources of OH reached their maximum around 12:00, while $P_{(O_3-OH)}$ was approximately two times of that of $P_{(HONO-OH)}$. On average, the OH production rates by photolysis of HONO and O_3 were 3.7×10^6 cm^{-3} s^{-1} and 4.9×10^6 cm^{-3} s^{-1}, respectively. In daytime, the sum of OH production rates by ozonolysis of alkenes was 3×10^5 cm^{-3} s^{-1}, which is much smaller than that of HONO and O_3. This value (3×10^5 cm^{-3} s^{-1}) was comparable to the results in previous studies (Kim et al., 2014; Ge et al., 2021; Martinez et al., 2003; Ren et al., 2003; Lee et al., 2016; Alicke et al., 2002; Kleffmann et al., 2005; Ren et al., 2013), but smaller than some other studies (Shi et al., 2020b; Zheng et al., 2020; Heard et al., 2004). Table 2 summarizes the OH production rate from HONO and O_3 photolysis from previous studies worldwide. It can be seen that $P_{(HONO-OH)}$ are larger than $P_{(O_3-OH)}$ in most of the observations, but sometimes the opposite is reported. Apparently, the relative importance of $P_{(HONO-OH)}$ and $P_{(O_3-OH)}$ strongly depends on the ratio of $HONO/O_3$. Especially in winter, photolysis of HONO tends to be the predominant OH source due to the low concentration of O_3 and water vapor.

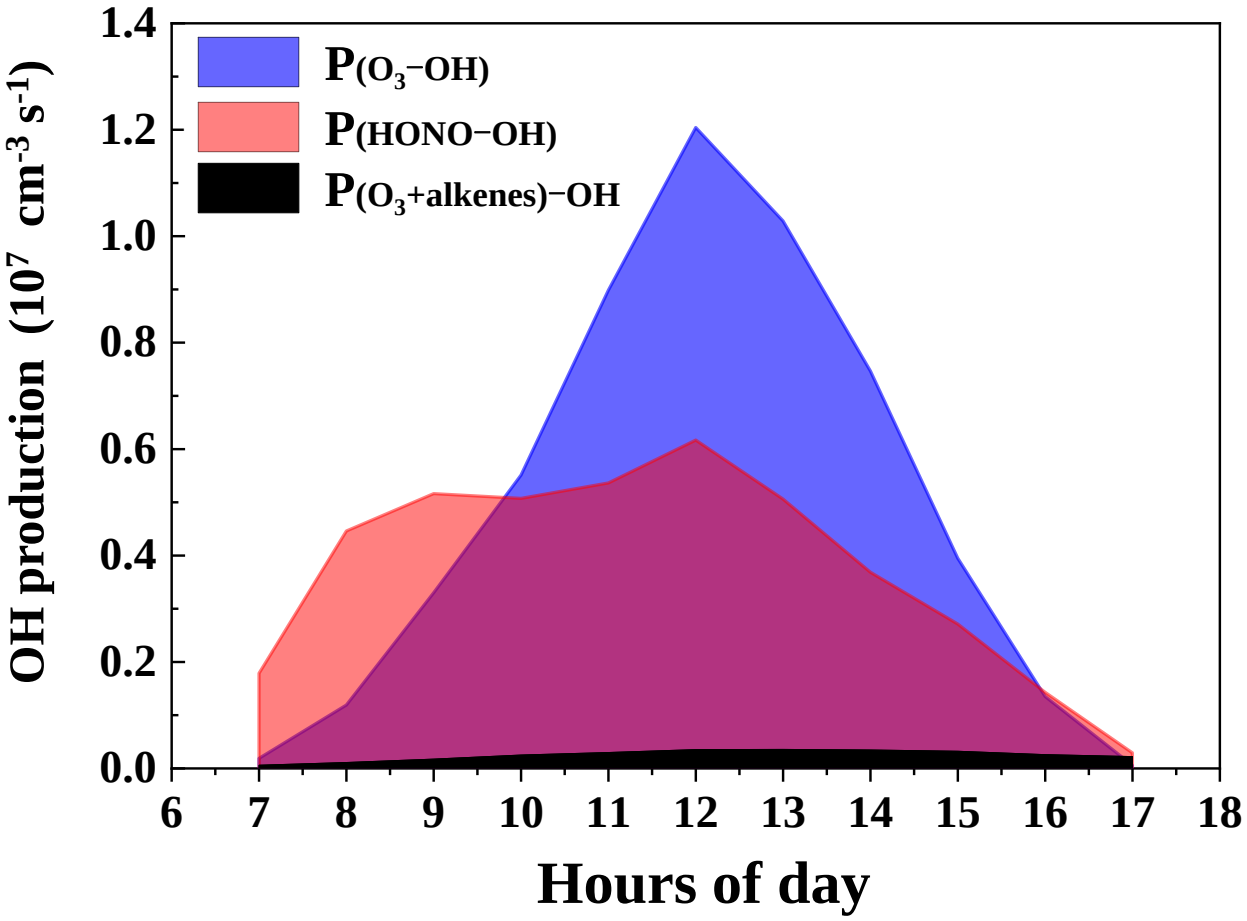


Figure 9. The yield and comparison of OH radicals by HONO, O_3 and ozonolysis of alkenes.

Table 2. The OH production rates from HONO and O_3 photolysis in previous observations.

Location	Date	Season	$P_{(HONO–OH)}$ (ppbv h^{-1})	$P_{(O3–OH)}$ (ppbv h^{-1})	Reference
New York, USA	Jun–Jul 1998	Summer	0.10	0.22	1
Nashville, USA	Jun–Jul 1999	Summer	0.29	0.33	2
Birmingham, UK	Jan–Feb 2000	Winter	0.45	0.01	3
New York, USA	Jun–Aug 2001	Summer	0.81	0.19	4
Santiago, Chile	May–Jun 2005	Winter	2.90	0.01	5
	Mar 2005	Summer	1.70	0.13	
El Arenosillo, Spain	Dec 2008	Winter	0.11	0.09	6
Colorado, USA	Feb–Mar 2011	Winter	0.45	0.04	7
Beijing, China	Sep–Oct 2004	Autumn	1.31	0.18	8
Xinken, China	Oct–Nov 2004	Autumn	3.66	0.88	9
Back Garden, China	Jul 2006	Summer	1.32	2.20	10
Yufa, China	Aug 2006	Summer	1.68	0.38	11
Tung Chung, China	Aug 2011	Summer	1.50	0.90	12
Wangdu, China	Jun 2014	Summer	1.68	1.20	13
Hong Kong, China	Mar–May 2015	Spring	6.40	a	14
Changzhou, China	Dec 2015	Winter	1.04	0.36	15
Guangzhou, China	Oct 2015	Autumn	1.24	0.41	16
	Jul 2016	Summer	0.71	0.44	
Ji'nan, China	Aug 2016	Summer	1.88	0.63	17
Changzhou, China	Apr 2017	Spring	1.66	2.78	18
Mount Tai, China	Dec 2017	Winter	0.52	0.02	19
	Mar–Apr 2018	Spring	0.51	0.18	
Nanjing, China	Nov–Nov 2017/2018	A year	1.16	0.41	20
Gucheng, China	Jan–Feb 2018	Winter	1.40	0.01	21
Guangzhou, China	Sep–Nov 2018	Autumn	0.54	0.72	22

a: far less than $P_{(HONO–OH)}$.

Reference: 1. Zhou et al. (2002a); 2. Martinez et al. (2003); 3. Heard et al. (2004); 4. Ren et al. (2003); 5. Elshorbany et al. (2010); 6. Sörgel et al. (2011a); 7. Kim et al. (2014) ; 8. An et al. (2009); 9. Su et al. (2008b); 10. Su (2008); 11. Yang et al. (2014); 12. Xue et al. (2016); 13. Liu et al. (2019a); 14. Yun et al. (2017); 15. Zheng et al. (2020); 16. Yang et al. (2017a); 17. Li et al. (2018a); 18. Shi et al. (2020a); 19. Jiang et al. (2020); 20. Liu et al. (2019b); 21. (Li in preparation); 22. This study

3.5 Box model simulation of HONO impact on atmospheric oxidation capacity

Atmospheric oxidation capacity refers to the total removal rates of CO and VOCs by major oxidants (e.g., OH, NO_3 and O_3) (Elshorbany et al., 2010; Xue et al., 2016; Tan et al., 2019b). As the primary oxidant in the atmosphere, the OH concentration is widely used to quantitatively describe the atmospheric oxidation capacity (Zheng et al., 2020; Liu et al., 2021; Shi et al., 2020b; Zhang et al., 2019a). And ozone is another indicator of atmospheric oxidation capacity. A box model (MCMv3.3.1) was conducted to simulate OH and O_3 concentrations with and without HONO constrained with observational data. Figure S5 shows the time series of measured and simulated O_3 concentrations. The model performance was evaluated to be good by the index of agreement (IOA) (see Supplementary infomation). It should be noted that the box model ignores the influence of transport and convection, so the simulated O_3 concentration does not represent the actual O_3 concentration in the atmosphere.

The time series of simulation results of O_3 and OH can be found in Fig. S6. Figure 10 shows diurnal variations of simulated O_3 and OH with and without HONO constrained. Daytime maximum OH concentration with HONO (6.1×10^6 cm^{-3}) was simulated to be 59% higher than the simulation without HONO (3.9×10^6 cm^{-3}), and the daily maximum concentration of O_3 with HONO (43.2 ppbv) was simulated to be 68.8% higher than the simulation without HONO (25.6 ppbv). These results are both within the range of prior studies (Elshorbany et al., 2012; Fu et al., 2019; Gil et al., 2021; Liu et al., 2021; Malkin et al., 2016; Xue et al., 2020; Yang et al., 2021a; Yun et al., 2017; Zhang et al., 2016), suggesting a strong HONO enhancement effect on atmospheric oxidation capacity. In addition, the impact of HONO on O_3 appeared two hours later than on OH, likely reflecting that HO_2 and RO_2, which are key proxy radicals in O_3 production were not significantly higher during early morning hours, despite higher HONO and OH.

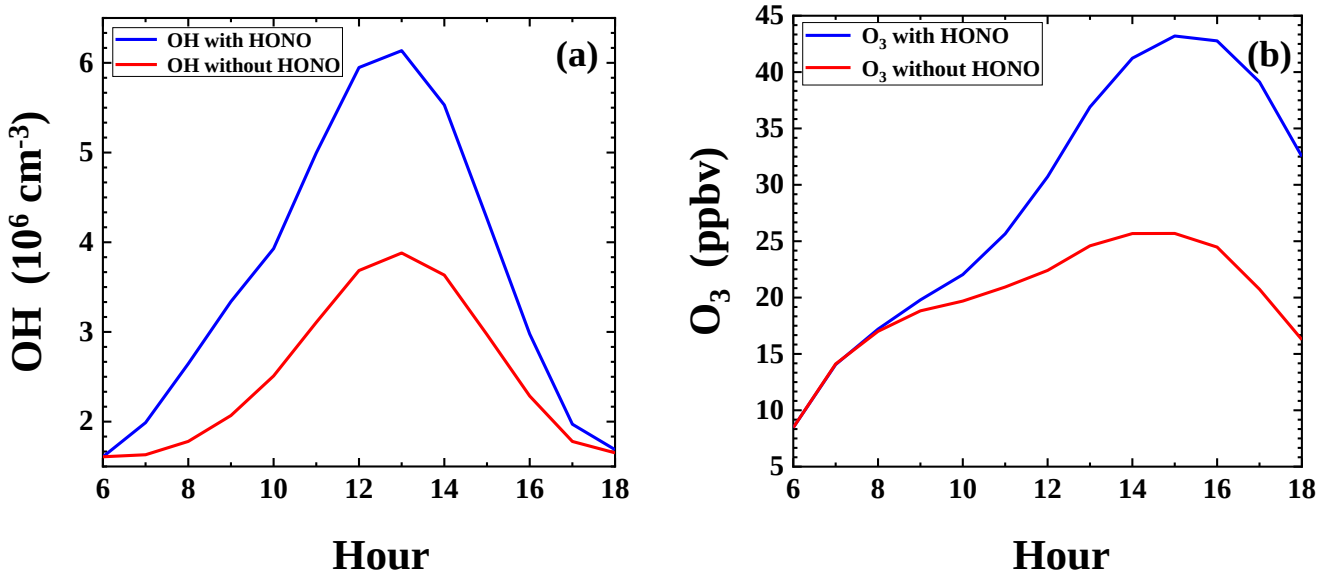


Figure 10. The diurnal variations of simulated O_3 and OH output with and without the HONO constrained in model.

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. The emission ratios (HONO/NOx) were derived from an analysis of 11 fresh plumes, varying 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 OH + NO at night was 0.26 ± 0.08 ppbv h^{-1}, which can be seen as secondary results from primary emission. They were both much higher than the observed increase rate of HONO (0.02 ppbv h^{-1}) during the night. Nighttime soil emission rate was calculated to be 0.019 ± 0.001 ppbv h^{-1}, which is comparable to the observed increase rate of HONO during night, thus further demonstrating the importance of direct emissions. In order to balance the nighttime HONO budget and assuming dry deposition to be the principle loss process, a dry deposition rate of at least 1.8 cm s^{-1} is required. Correlation analysis shows that the heterogeneous reaction of NO_2

related to NH_3 and RH may contribute to the nighttime HONO formation. 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 the primary emission P_{emis} at 0.12 ± 0.01 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 should not be as important as ground as a heterogenous reaction media, as very weak correlation between $P_{Unknown}$ and $PM_{2.5}$. Moreover, no correlations were found between $P_{Unknown}$ and nitrate/HNO_3, NH_3, SO_2. We assessed the role of HONO in the production of OH and O_3 by calculating OH production rate as well as by simulating the chemistry with a box model (MCMv3.3.1). The average net formation rate of OH attributed to HONO, O_3 and ozonolysis of alkenes was 3.7×10^6 cm^{-3} s^{-1}, 4.9×10^6 cm^{-3} s^{-1} and 3×10^5 cm^{-3} s^{-1}, respectively. Box model simulations confirmed strong HONO enhancement effect on OH and O_3 by 59% and 68.8%, respectively.

Data availability

HONO data, other trace gases data and meteorological data are available upon request from the corresponding author.

Contribution

Yihang Yu: Validation, Formal analysis, Writing - Original Draft, Visualization. **Peng Cheng:** Conceptualization, Methodology, Writing - Review & Editing, Supervision, Project administration, Funding acquisition. **Huirong Li:** Validation, Formal analysis, Investigation, Data Curation. **Wenda Yang:** Software, Investigation, Data Curation. **Baobin Han:** Investigation. **Wei Song:** Resources. **Weiwei Hu:** Resources. **Xinming Wang:** Resources. **Bin Yuan:** Resources. **Min Shao:** Resources. **Zhijiong Huang:** Resources. **Zhen Li:** Resources. **Junyu Zheng:** Resources. **Haichao Wang:** Writing - Review & Editing. **Xiaofang Yu:** Investigation.

Competing interests

The authors declare that they have no conflict of interest.

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