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Variations and sources of nitrous acid (HONO) during a severe pollution episode in Beijing in winter 2016

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1 **Abstract**

2 HONO is an important precursor of OH radical and plays a key role in atmospheric chemistry, but its
3 source and formation mechanism remain uncertain, especially during complex atmospheric pollution
4 processes. In this study, HONO mixing ratios were measured by a custom-made instrument during a
5 severe pollution event from 16 to 23 December 2016, at an urban area of Beijing. The measurement
6 was divided into three periods: I (haze), II (severe haze) and III (clean), according to the levels of
7 PM_{2.5}. This pollution episode was characterized by high levels of NO (75 ± 39 and 94 ± 40 ppbV
8 during periods I and II, respectively) and HONO (up to 10.7 ppbV). During the nighttime, the
9 average heterogeneous conversion frequency during the two haze periods were estimated to be
10 0.0058 and 0.0146 h⁻¹, and it was not the important way to form HONO. Vehicle emissions
11 contributed 52% (± 16)% and 40% (± 18)% to ambient HONO at nighttime during periods I and II.
12 The contribution of homogeneous reaction of NO with OH should be reconsidered under high-NO_x
13 conditions and could be noticeable to HONO sources during this pollution event. Furthermore,
14 HONO was positively correlated with PM_{2.5} during periods I and II, suggesting a potential chemical
15 link between HONO and haze particles.

16 **Key words:** Nitrous acid measurement, Haze, Vehicle emissions, Homogeneous reaction, Daytime
17 HONO budget

18 **1. Introduction**

19 Hydroxyl (OH) radical is a major oxidant in the troposphere and plays an important role in the ability
20 of the atmosphere to “cleanse itself” (Heard and Pilling, 2003). In addition, OH radical affects many
21 chemical and photochemical processes and contributes to the formation of O₃ and PANs (peroxyacyl
22 nitrates) (Heard and Pilling, 2003; Hofzumahaus et al., 2009). As an important precursor of OH

23 radical, HONO is a significant species in the tropospheric photochemistry (Alicke et al., 2002;
24 Kleffmann et al., 2005; Lammel and Cape, 1996). Recent studies proposed that HONO photolysis
25 (R1) produced 34% ~ 56% of OH radical in the whole daytime (Alicke et al., 2002; Hendrick et al.,
26 2014; Kleffmann, 2007; Michoud et al., 2012) and produced about 80% of OH radical in the early
27 morning (Acker et al., 2006). Moreover, in pollution episodes, OH radical is almost generated by
28 HONO photolysis (Aumont et al., 2003; Platt and Perner, 1980).



30 In recent years, HONO has been extensively discussed owing to its ability of initiating and
31 accelerating daytime photochemistry. HONO sources were generally grouped into direct emissions,
32 homogeneous reactions, heterogeneous reactions, surface-absorbed nitric acid and/or particulate
33 nitrate photolysis and soil nitrite emissions (Spataro and Ianniello, 2014, and references therein).
34 Although vehicle emissions contribute to ambient HONO, the relative contribution is controversial,
35 as there are different types of vehicles and various vehicle emission standards (Trinh et al., 2017).
36 The reaction of NO with OH (R2) is widely accepted as a key homogeneous pathway to form HONO,
37 especially when NO and OH are high during the daytime in polluted areas (e.g. Li et al., 2012). Due
38 to the low level of OH radical, this homogeneous reaction was reported to be insignificant during the
39 nighttime (Wong et al., 2011). However, recent studies found that nocturnal OH radical were
40 relatively high in China, for example, OH radical was mostly above $3 \times 10^5 \text{ cm}^{-3}$ in Wangdu in
41 summer 2014. Therefore, homogeneous formation **could** play an important role in HONO formation
42 (Tan et al., 2017; Tong et al., 2015). Laboratory studies suggested that heterogeneous conversion of
43 NO_2 into HONO is an important HONO source (Ammann et al., 1998; Broske et al., 2003;
44 Finlayson-Pitts et al., 2003; George et al., 2005; Kleffmann et al., 1999; Stemmler et al., 2007), but

45 the exact mechanisms are unclear. Although substantial field and laboratory studies were carried out
46 to investigate formation mechanisms of HOHO in the troposphere, HOHO sources and their relative
47 contributions to ambient HONO are still unclear, especially under pollution conditions.



49 Beijing, a rapidly developing megacity in China, has been suffering from haze pollution for several
50 years. For example, only during January 2013, the PM_{2.5} level in the urban area of Beijing exceeded
51 the Second Grade National Standard of China (75 μg m⁻³) for 22 days, meaning that people were
52 exposed to polluted air for nearly the whole month (He et al., 2014). Although the government
53 rapidly took the strict control measures for anthropogenic emissions, such as vehicle control and
54 production restriction measures, substantial amounts of haze events have occurred since 2013. Haze
55 is usually caused by secondary aerosol particles (Guo et al., 2014; Huang et al., 2014; Liu et al.,
56 2017a). Several studies indicated that high level of HONO produced high level of OH radical,
57 resulting in increased secondary aerosols (An et al., 2013; Huang et al., 2014). Therefore, the source
58 and formation mechanism of HONO are crucial for better understanding the atmospheric chemistry
59 during pollution episodes. Numerous field observations were performed to investigate mixing ratios
60 and potential sources of HONO in Beijing (shown in Table 1), but the studies for the level and
61 formation mechanism of HONO during haze episodes are still limited.

62 Beijing has suffered from a severe haze pollution from 16 to 21 December, in winter 2016. The
63 government issued the first red alert for heavy air pollution in 2016, and rapidly took the most strict
64 control measures for anthropogenic emissions, such as vehicle control and production restriction
65 measures. Hereby, we performed a field measurement of HONO at an urban area of Beijing during
66 16 to 23 December 2016, including this severe pollution process. Simultaneous trace gases (SO₂, CO,

67 NO, NO₂ and O₃), PM_{2.5}, and meteorological parameters were also obtained in this measurement.
 68 The objectives of this study are to explore levels and variations of HONO and to evaluate relative
 69 contributions of different HONO sources during this pollution event in Beijing.

70 **Table 1.** HONO measurements in Beijing.

Date	Type	HONO/ppbV	reference
May. Jun-Jul. Sep. Dec. 2000	urban	0.7 - 3.0	(Hu et al., 2002)
Jul.-Aug. 2002/2003	urban	1.72	(Wu et al., 2009)
Aug.-Sep. 2004	urban	0.4 - 6.1	(Qin et al., 2006)
9-10 Feb. 2007	urban	0.15 - 9.71	(Spataro et al., 2013)
Jul. 2008-Apr. 2009	urban	0.19 (spring)	(Hendrick et al., 2014)
		0.18 (summer)	
		0.46 (autumn)	
		0.48 (winter)	
22 Feb.-2 Mar. 2014	urban	0.49 - 3.24 (severe haze)	(Hou et al., 2016)
		0.28 - 1.52 (clean)	
28 Oct.-2 Nov. 2014	urban	0.54 - 2.77	(Tong et al., 2015)
	suburban	0.18 - 1.23	
12-22 Dec. 2015	urban	1.34 (haze)	(Tong et al., 2016)
		0.51 (non-haze)	
	suburban	0.79 (haze)	
		0.44 (non-haze)	
22 Sep. 2015- 25 Jul. 2016	urban	2.27 (autumn)	(Wang et al., 2017)
		1.05 (winter)	
		1.05 (spring)	
		1.38 (summer)	

71 **2. Experimental**

72 **2.1. Measurement site**

73 The atmospheric HONO mixing ratios and meteorological parameters were measured on the
74 third floor of No.2 building (~ 10 meters above the ground level) at Institute of Chemistry, Chinese
75 Academy of Sciences (ICCAS, 39°59'22.68"N, 116°19'21.58"E) in Beijing. About 480 meters to the
76 south is the Fourth Ring Road. It is a typical urban site and was described in details in previous
77 works (Hou et al., 2016; Tong et al., 2016; Tong et al., 2015). The observation was performed from
78 16 to 23 December 2016, including a pollution period and a following clean period. In addition,
79 mixing ratios of trace gases (including SO₂, CO, NO, NO₂ and O₃) and PM_{2.5} were simultaneously
80 acquired from Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences
81 (RCEES, 40°00'28"N, 116°20'15"E), 2.8 kilometers northeast from the ICCAS site, which is also
82 adjacent to the Fourth Ring Road and has similar conditions with few spatial differences of NO₂ and
83 NO_x levels from the ICCAS site. Black carbon was measured at the Tower Branch of the Institute of
84 Atmospheric Physics, Chinese Academy of Sciences (IAP, 39°58'54.9078"N, 116°23'4.7904"E),
85 about 5 kilometers southeast from the ICCAS site. The IAP site is between the North Third and
86 Fourth Ring Roads, which is surrounded by condensed population and heavy traffic, and thus it is a
87 typical urban area of Beijing, similar to two sites above.

88 **2.2. Measurement instruments**

89 The atmospheric HONO mixing ratios were conducted using a custom-made HONO analyzer which
90 was described in details elsewhere (Hou et al., 2016; Tong et al., 2016; Tong et al., 2015). Briefly, the
91 principle of HONO analyzer is similar to long path absorption photometer (LOPAP) (Heland et al.,
92 2001; Kleffmann et al., 2002). HONO is fast collected by a two-channel glass stripping coil with an

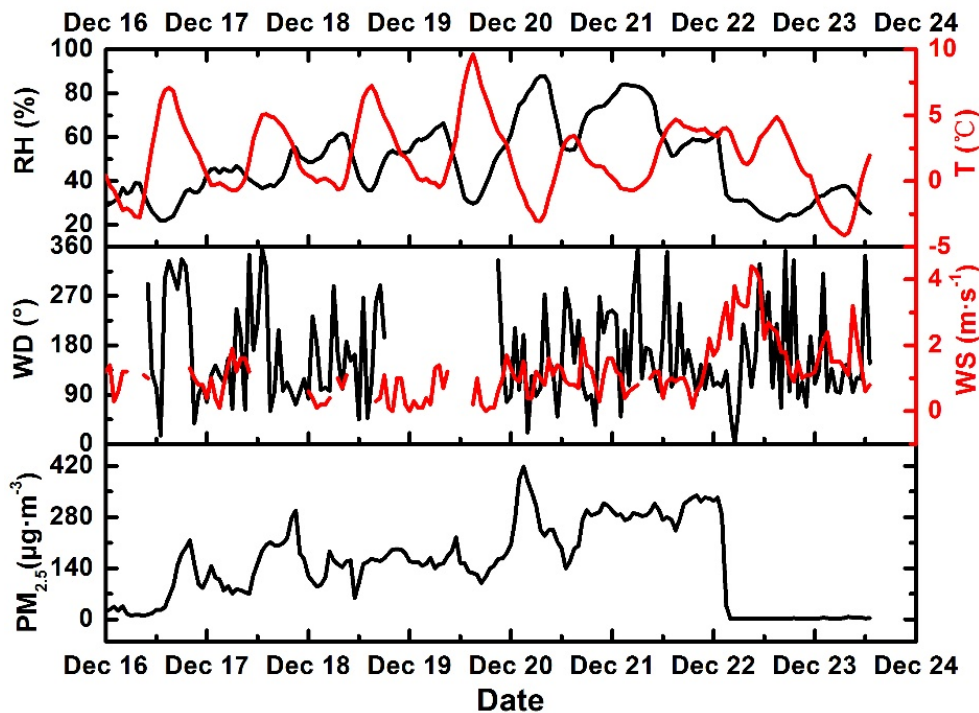
93 absorption solution (0.06 M sulfanilamide in 1 M HCl) to form a stable diazonium salt which then
94 reacts with a dye solution [0.8 mM N-(1-naphthyl) ethylenediamine-dihydrochloride]. Then an azo
95 dye is formed and finally pumped into a 50 cm liquid waveguide capillary cell (LWCC). A
96 subsequent detection is performed by an optical absorption spectrometer (Ocean Optics, SD2000).
97 The final HONO concentration is the difference of signals between the two channels. The liquid flow
98 rate is 0.3 mL min⁻¹ with a sampling gas flow rate of 1.0 L min⁻¹. The detection limit of the
99 instrument is 200 pptV with a response time of 15 minutes. A side by side intercomparison between
100 the custom-made HONO analyzer and a commercial LOPAP instrument was carried out in our
101 previous study, which certified the accuracy and reliability of HONO analyzer (Hou et al., 2016).
102 The meteorological parameters consisting of air temperature (T), relative humidity (RH), wind speed
103 (WS) and wind direction (WD) were measured by a vaisala weather transmitter (WXT520). The
104 mixing ratios of SO₂, CO, NO, NO₂, NO_x and O₃ were determined using SO₂ analyzer (Thermo
105 Scientific, Model 43i), CO analyzer (Thermo Scientific, Model 48i), NO_x analyzer (Thermo
106 Scientific, Model 42i) and O₃ analyzer (Thermo Scientific, Model 49i) with detection limits of
107 1ppbV, 0.05ppmV, 1ppbV and 1ppbV, respectively. Black Carbon was measured using an AE-33
108 seven-wavelength Aethalometer.

109 **3. Results and discussion**

110 **3.1. Temporal variations of meteorological parameters and gaseous species**

111 Fig. 1 gives an overview of PM_{2.5} and meteorological parameters. The levels of PM_{2.5} were used to
112 classify the measurement into three periods. Period I was a haze period from 16 to 19 December
113 when PM_{2.5} were mostly higher than 75 µg m⁻³ with a mean value of 130 µg m⁻³, the RH ranged from
114 22% to 66% and wind speed was from 0 to 1.9 m s⁻¹. Period II was from 20 to 21 December, called a

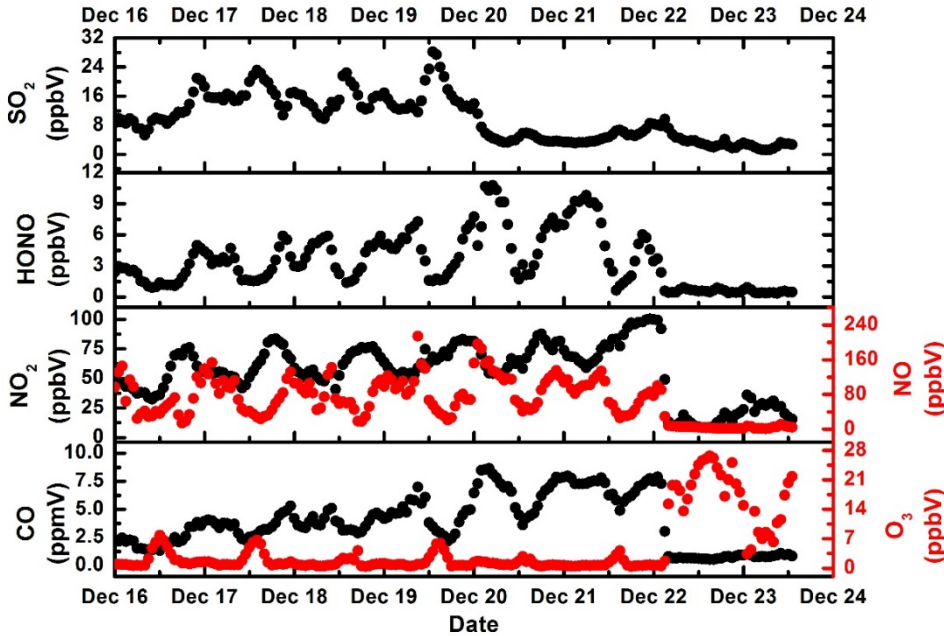
115 severe haze period with $PM_{2.5}$ between 140 and 418 $\mu\text{g m}^{-3}$ and the mean value of 285 $\mu\text{g m}^{-3}$. The
 116 RH during period II was between 69% and 88% and wind speed was from 0.1 to 2.2 m s^{-1} . During
 117 two haze periods, the wind speed was mostly less than 2.0 m s^{-1} . Due to the strong winds during
 118 period III from 22 to 23 December, the air was clean with $PM_{2.5}$ less than 10 $\mu\text{g m}^{-3}$ and the RH less
 119 than 30%. Moreover, the RH was negatively correlated with the ambient temperature in general. And
 120 most of the observed days had southerly winds, except for 22 December with a strong wind blowing
 121 from north-east.



122
 123 **Fig. 1.** Temporal trends of hourly average RH, T, WD, WS and $PM_{2.5}$ during the measurement.

124 The temporal variations of measured trace gases are illustrated in Fig. 2. All the data are hourly
 125 averaged. This pollution episode was characterized by high levels of NO_x . The mixing ratios of NO
 126 were extremely high with a maximum of 214 ppbV and a mean mixing ratio of 67 ppbV. The NO_2
 127 mixing ratios simultaneously ranged from 8 to 100 ppbV with a mean mixing ratio of 56 ppbV. The
 128 SO_2 mixing ratios varied from 1 to 28 ppbV with a mean mixing ratio of 10 ppbV. The mixing ratios

129 of O₃ and CO varied from 0 to 27 ppbV and 0 to 8.6 ppmV, respectively. HONO varied from 0.3 to
 130 10.7 ppbV with a mean mixing ratio of 3.5 ppbV, higher than those in previous observations (Hou et
 131 al., 2016; Spataro et al., 2013; Wang et al., 2017) in Beijing.



132
 133 **Fig. 2.** Temporal variations of hourly average SO₂, HONO, NO₂, NO, CO and O₃ during the
 134 measurement.

135 Table 2 shows mean mixing ratios of trace gases during the three periods. The highest mixing ratios
 136 of HONO, NO, NO₂, and CO were found during period II, followed by period I and period III. On
 137 the contrary, the O₃ mixing ratios were highest during period III. Furthermore, the SO₂ mixing ratios
 138 during period I was much higher than those during period II, with the peak being a factor of ~3
 139 higher, which might be due to the conversion of SO₂ to sulfate (Ma et al., 2018).

140 **Table 2.** Mean mixing ratios of trace gases during the three periods.

Trace Gases	I (Haze)	II (Severe haze)	III (Clean)	Total
	16-19 Dec.	20-21 Dec.	22-23 Dec.	16-23 Dec.
HONO (ppbV)	3.4 ± 1.7	5.8 ± 3.0	0.5 ± 0.2	3.5 ± 2.7
NO ₂ (ppbV)	60 ± 13	76 ± 14	19 ± 9	56 ± 23

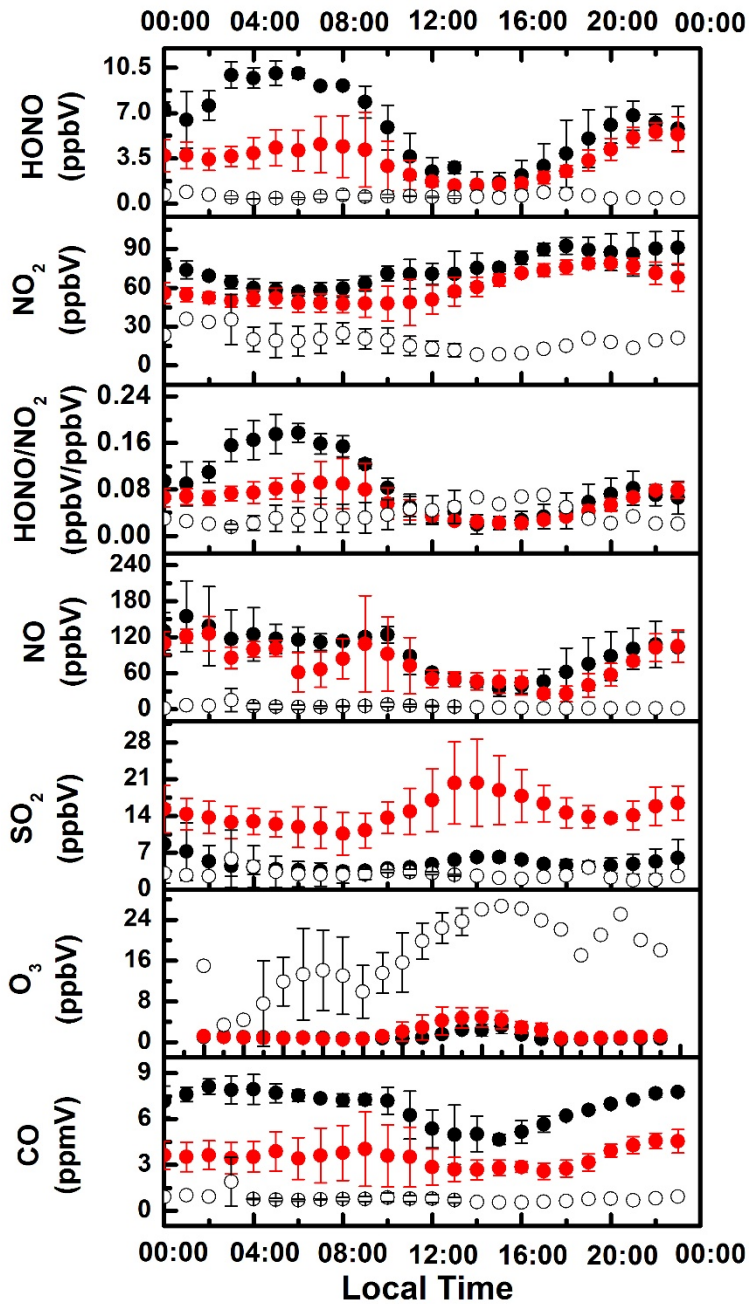
NO (ppbV)	75 ± 39	94 ± 40	5 ± 5	67 ± 48
SO ₂ (ppbV)	15 ± 4	5 ± 2	3 ± 1	9 ± 6
O ₃ (ppbV)	2 ± 2	1 ± 1	16 ± 7	4 ± 7
CO (ppmV)	3.5 ± 1.2	6.8 ± 1.2	0.8 ± 0.4	3.9 ± 2.3

141 3.2. Diurnal variations of gaseous species

142 Fig. 3 illustrates diurnal variations of average HONO, NO₂, NO, SO₂, O₃ and CO during the
143 measurement. The diurnal trends of HONO during the two haze periods I and II were noticeable
144 while those during period III were insignificant, contrary to the measurement in 2014 (Hou et al.,
145 2016) when the variations during clean period were more visible. Such low and stable levels of
146 HONO during period III in this study might be attributed to the strong wind which can accelerate
147 HONO vertical and horizontal mixing. During periods I and II, HONO peaked at around 07:00 LT
148 (local time) (4.6 ppbV) and at around 05:00 LT (10.0 ppbV), respectively. Then HONO mixing ratios
149 gradually decreased, caused by increased HONO photolysis rates and vertical mixing after sunrise
150 (Hendrick et al., 2014). The HONO mixing ratios dropped to minimums (~ 1.4 ppbV) at around
151 14:00 LT and then accumulated throughout the rest of the day. HONO had a rising process in the
152 evening due to the absence of photolytic loss, the decrease of the boundary layer height and/or strong
153 nocturnal HONO sources (Hendrick et al., 2014). High levels of HONO were found at nighttime.
154 HONO mixing ratio during both periods I and II showed a small decrease before midnight and then
155 increased again from midnight, suggesting potential additional sources. The average diurnal cycles of
156 HONO displayed nocturnal or early-morning maximums and daytime minimums during periods I
157 and II, similar to those in previous studies (Huang et al., 2017; Tong et al., 2016; Wang et al., 2017).
158 The diurnal variations of NO, NO₂, and CO were weak and mixing ratios of these gaseous species
159 were extremely low during period III, due to strong winds. Additionally, diurnal values of NO and

160 CO followed the same pattern during periods I and II, and peaked at around 9:00 LT due to vehicle
161 emissions during the morning rush hour, subsequently declined to minimums at around 15:00 LT.
162 After 16:00 LT, NO and CO mixing ratios began to rise due to the evening rush hour and the
163 reduction of the boundary layer depth after sunset (Hendrick et al., 2014; Tong et al., 2016). The NO₂
164 mixing ratios were generally stable and after 12:00 LT gradually increased during periods I and II.
165 But NO₂ mixing ratios exhibited no obvious variations and remained at low levels during period III.
166 SO₂ mixing ratios peaked at around 14:00 LT during two haze periods and their diurnal patterns were
167 more significant during period I than during period II.

168 According to the descriptions of section 3.1 and 3.2, the wind speed was relatively low during
169 periods I and II, suggesting a limited from regional contribution. However, wind speed was mostly
170 higher than 2.0 m s⁻¹ during period III, and severely affected the in situ parameters and thus the data
171 points during period III were not discussed for further analysis of HONO sources in the following
172 sections.



- severe haze period
- haze period
- clean period

173

174 **Fig. 3.** Diurnal variations of average HONO, NO₂, NO, SO₂, O₃ and CO during periods I (haze), II

175 (severe haze) and III (clean). The error bars represent the standard deviation during the measurement.

176 **3.3. Nocturnal HONO sources**

177 **3.3.1 Contribution of homogeneous processes**

178 The net HONO production ($P_{\text{OH}+\text{NO}}^{\text{net}}$) of homogeneous processes during the nighttime is calculated by

179 the following equation.

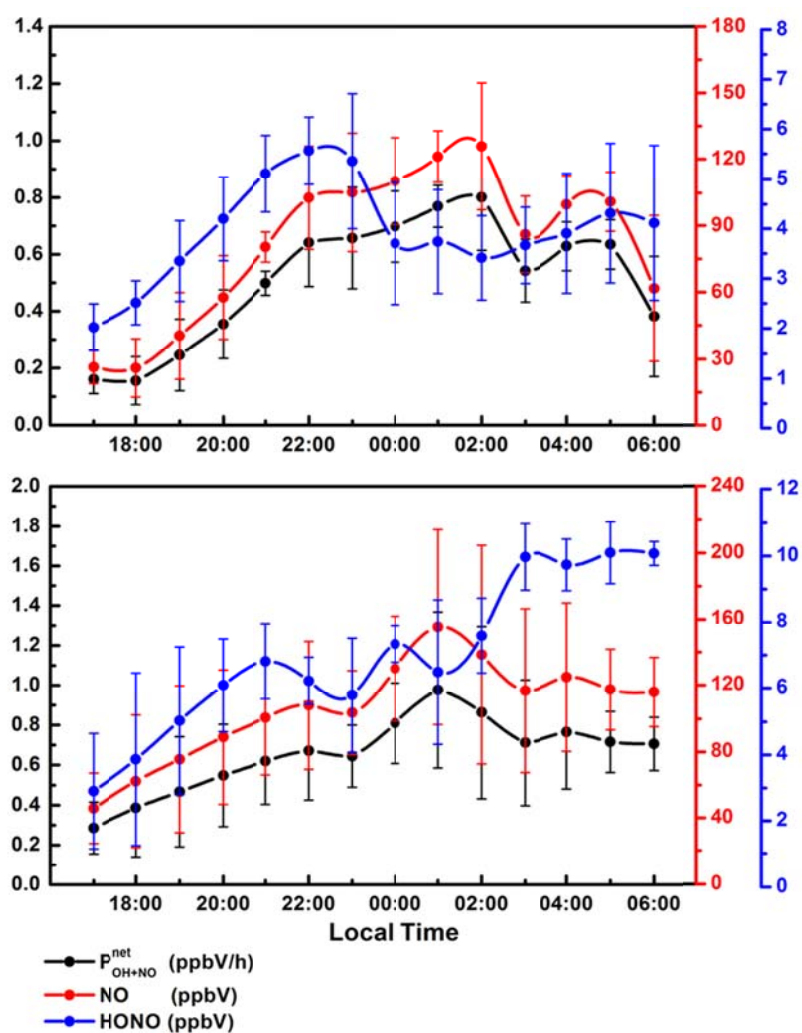
$$180 \quad P_{\text{OH}+\text{NO}}^{\text{net}} = k_{\text{OH}+\text{NO}}[\text{OH}][\text{NO}] - k_{\text{OH}+\text{HONO}}[\text{OH}][\text{HONO}] \quad (1)$$



182 The rate constants $k_{\text{OH}+\text{NO}}$ and $k_{\text{OH}+\text{HONO}}$ are 7.2×10^{-12} and 5.0×10^{-12} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, for reaction
183 R2 and R3 at 298 K, respectively (Li et al., 2012). [NO] and [HONO] are hourly average mixing
184 ratios of NO and HONO, respectively. $k_{\text{OH}+\text{NO}}$ and $k_{\text{OH}+\text{HONO}}$ are similar, hence NO and HONO play
185 key roles in calculating $P_{\text{OH}+\text{NO}}^{\text{net}}$. [OH] is the OH radical concentration which was not available
186 during the measurement, and thus an estimate is made. Tan et al. (2017) observed that the mean value
187 of the nighttime OH was 5×10^5 molecules cm^{-3} in summer 2014 in Wangdu. And here 2.5×10^5
188 molecules cm^{-3} was used, since the $[\text{OH}]_{\text{summer}}/[\text{OH}]_{\text{winter}}$ ratio is about 2 (Spataro et al., 2013, and
189 references therein). The nocturnal variations of $P_{\text{OH}+\text{NO}}^{\text{net}}$, HONO and NO during periods I and II are
190 illustrated in Fig. 4. Generally, the variations of $P_{\text{OH}+\text{NO}}^{\text{net}}$ followed those of NO due to extremely
191 high NO levels governing the variations of $P_{\text{OH}+\text{NO}}^{\text{net}}$ during the two haze periods. During period I,
192 $P_{\text{OH}+\text{NO}}^{\text{net}}$ varied from 0.09 to 0.98 ppbV h^{-1} , and increased before midnight while decreased gradually
193 after midnight. During period II, $P_{\text{OH}+\text{NO}}^{\text{net}}$ ranged from 0.19 to 1.25 ppbV h^{-1} which increased before
194 midnight but decreased after midnight and then almost kept constant. This result implied that the
195 nocturnal HONO source from homogeneous processes was much larger during period II than that
196 during period I. The level of $P_{\text{OH}+\text{NO}}^{\text{net}}$ during the two haze periods were higher than those in previous
197 study by Li et al. (2012) at a rural site in Southern China ($0 \sim 0.28 \text{ ppbV h}^{-1}$), but lower than our
198 previous study (2.18 ppbV/h at an urban area of Beijing) (Tong et al., 2015).

199 To estimate the contribution of homogeneous reaction of NO with OH, an episode (17:00 LT ~ 21:00
200 LT) is selected to integrate $P_{\text{OH}+\text{NO}}^{\text{net}}$ with increased HONO mixing ratios. The accumulated HONO

201 were 3.09 ppbV and 3.90 ppbV from 17:00 LT to 21:00 LT, during periods I and II, respectively. The
 202 integrated $P_{\text{OH+NO}}^{\text{net}}$ and the contributions of homogeneous processes are shown in Table S1. The
 203 HONO production from homogeneous reaction contributed 35% and 47% of accumulated HONO,
 204 during periods I and II, respectively. And twice and half of 2.5×10^5 molecules cm^{-3} were used for
 205 sensitivity studies (Lou et al., 2010) (shown in Table S1). It can be seen that HONO formation at
 206 nighttime due to OH and NO homogeneous reaction was highly dependent on the OH concentrations.



207
 208 **Fig. 4.** The nocturnal variations of hourly average $P_{\text{OH+NO}}^{\text{net}}$, HONO and NO during periods I and II.
 209 The error bars represent the standard deviation.

210 3.3.2. Heterogeneous conversion of NO_2

211 Numerous laboratory studies and field observations reported that heterogeneous conversion of NO_2

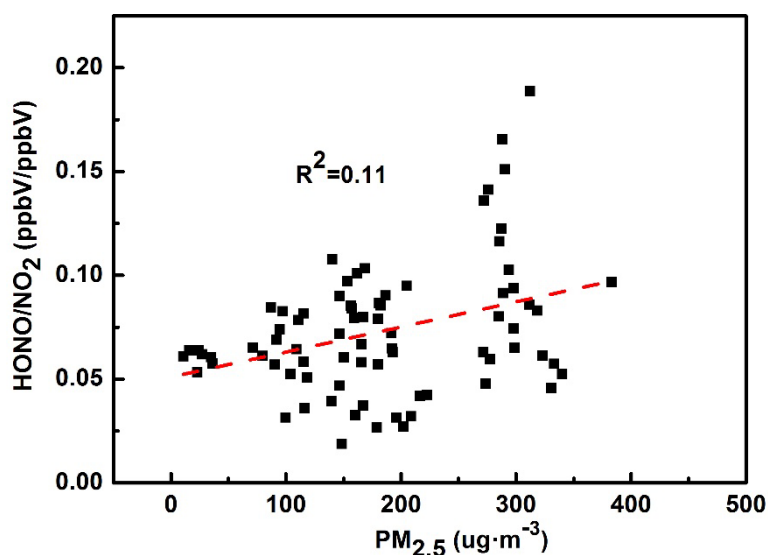
212 into HONO frequently occurred in the atmosphere (Spataro and Ianniello, 2014, and references
 213 therein). The nocturnal HONO/NO₂ ratios varied from 0.018 to 0.199 during the two haze periods,
 214 comparable to the ranges in previous studies (Alicke et al., 2002; Spataro et al., 2013; Tong et al.,
 215 2015). The mean values of HONO/NO₂ ratios were 0.064 and 0.095, during periods I and II
 216 respectively. HONO conversion frequency is another parameter to evaluate heterogeneous
 217 conversion of NO₂ into HONO and is calculated using the following equations and adopting CO and
 218 NO₂ as reference gases, as reported by previous studies (Su et al., 2008; Wang et al., 2017).

$$\begin{aligned}
 219 \quad C_{\text{HONO}}^{\text{X}} &= \frac{2\left(\frac{[\text{HONO}]_{t_2}}{[\text{X}]_{t_2}} \times \overline{[\text{X}]} - \frac{[\text{HONO}]_{t_1}}{[\text{X}]_{t_1}} \times \overline{[\text{X}]}\right)}{(t_2-t_1)\left(\frac{[\text{NO}_2]_{t_2}}{[\text{X}]_{t_2}} \times \overline{[\text{X}]} + \frac{[\text{NO}_2]_{t_1}}{[\text{X}]_{t_1}} \times \overline{[\text{X}]}\right)} \\
 220 \quad &= \frac{2\left(\frac{[\text{HONO}]_{t_2}}{[\text{X}]_{t_2}} - \frac{[\text{HONO}]_{t_1}}{[\text{X}]_{t_1}}\right)}{(t_2-t_1)\left(\frac{[\text{NO}_2]_{t_2}}{[\text{X}]_{t_2}} + \frac{[\text{NO}_2]_{t_1}}{[\text{X}]_{t_1}}\right)} \quad (2)
 \end{aligned}$$

$$221 \quad C_{\text{HONO}} = \frac{1}{3} (C_{\text{HONO}}^0 + C_{\text{HONO}}^{\text{CO}} + C_{\text{HONO}}^{\text{NO}_2}) \quad (3)$$

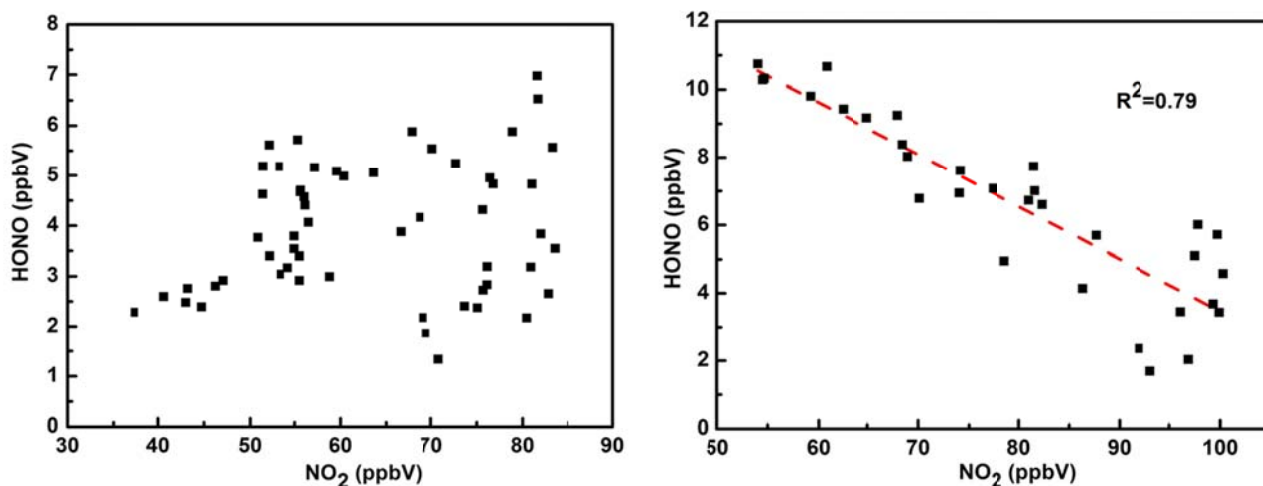
222 Where C_{HONO} is HONO conversion frequency from NO₂. $[\text{HONO}]_t$, $[\text{NO}_2]_t$ and $[\text{X}]_t$ represent mixing
 223 ratios of HONO, NO₂ and reference gases, respectively, at the measuring time t . $\overline{[\text{X}]}$ is the average
 224 mixing ratio of reference gas during the time interval of t_1 and t_2 , $C_{\text{HONO}}^{\text{X}}$ is the conversion
 225 frequency scaled with X and C_{HONO}^0 is the conversion frequency which is not scaled. The average
 226 C_{HONO} during periods I and II were 0.0058 and 0.0146 h⁻¹, respectively, which were comparable to
 227 previous works, such as 0.007 h⁻¹ in Shanghai (Wang et al., 2013), 0.008 h⁻¹ in Beijing (Wang et al.,
 228 2017), 0.014 h⁻¹ in Kathmandu (Yu et al., 2009), and 0.0091 h⁻¹ in Xi'an (Huang et al., 2017). The
 229 higher conversion efficiency of NO₂ heterogeneous reaction was found during period II, which might
 230 be attributed to higher RH (69% ~ 88%) (as seen in Fig. S1), since water absorbed on surfaces
 231 participated in the heterogeneous reaction of NO₂ to form HONO and several studies confirmed that
 232 surface adsorbed water was clearly related to the RH (Stutz et al., 2004, and references therein).

233 Besides the RH, aerosol surface as a media, is another important factor for heterogeneous conversion
234 of NO₂ (Huang et al., 2017; Li et al., 2012). As aerosol surface density is not available in this study,
235 PM_{2.5} concentrations are used as surrogates to estimate the influence of aerosol surface on the
236 heterogeneous conversion of NO₂ to HONO. The correlation of HONO/NO₂ with PM_{2.5}
237 concentrations is shown in Fig. 5. The positive correlation of HONO/NO₂ with PM_{2.5} indicated the
238 heterogeneous conversion of NO₂ into HONO on aerosol surfaces. However, the relative amount of
239 HONO formed on aerosol surfaces might be small due to the weak correlation ($R^2=0.11$).



240
241 **Fig. 5.** The correlation of HONO/NO₂ ratios with PM_{2.5} during periods I and II.

242 To further evaluate the contribution of NO₂ conversion, the nocturnal correlations between HONO
243 and NO₂ during periods I and II were illustrated in Fig. 6. There was no significant relationship
244 between HONO and NO₂ during period I while there was a significant negative correlation between
245 them ($R^2 = 0.79$) during period II. Theoretically, if NO₂ is a critical precursor of HONO, the positive
246 correlation between HONO and NO₂ should be found but that was not the case. This result can be
247 explained by that: some other sources were strong enough and thus they masked the contribution of
248 the NO₂ conversion.



249

250 **Fig. 6.** Correlations of HONO with NO₂ during periods I (left) and II (right).

251 **3.3.3. Contribution of direct emissions**

252 CO and NO are considered as primary pollutants emitted from combustion processes like burning of
 253 fossil fuels or biomass as well as vehicle emissions (Quan et al., 2014; Sun et al., 2014; Tong et al.,
 254 2016). In this study, good correlations of CO with NO at nighttime during the two haze periods were
 255 observed (Fig. S2), indicating that they had common sources. To avoid the influence of HONO

256 photolysis, only the data during the nighttime (from 17:00 LT to next 06:00 LT) was considered. As
 257 seen in Fig. 7, the correlations of HONO with CO and NO during the nighttime were 0.70 and 0.27,

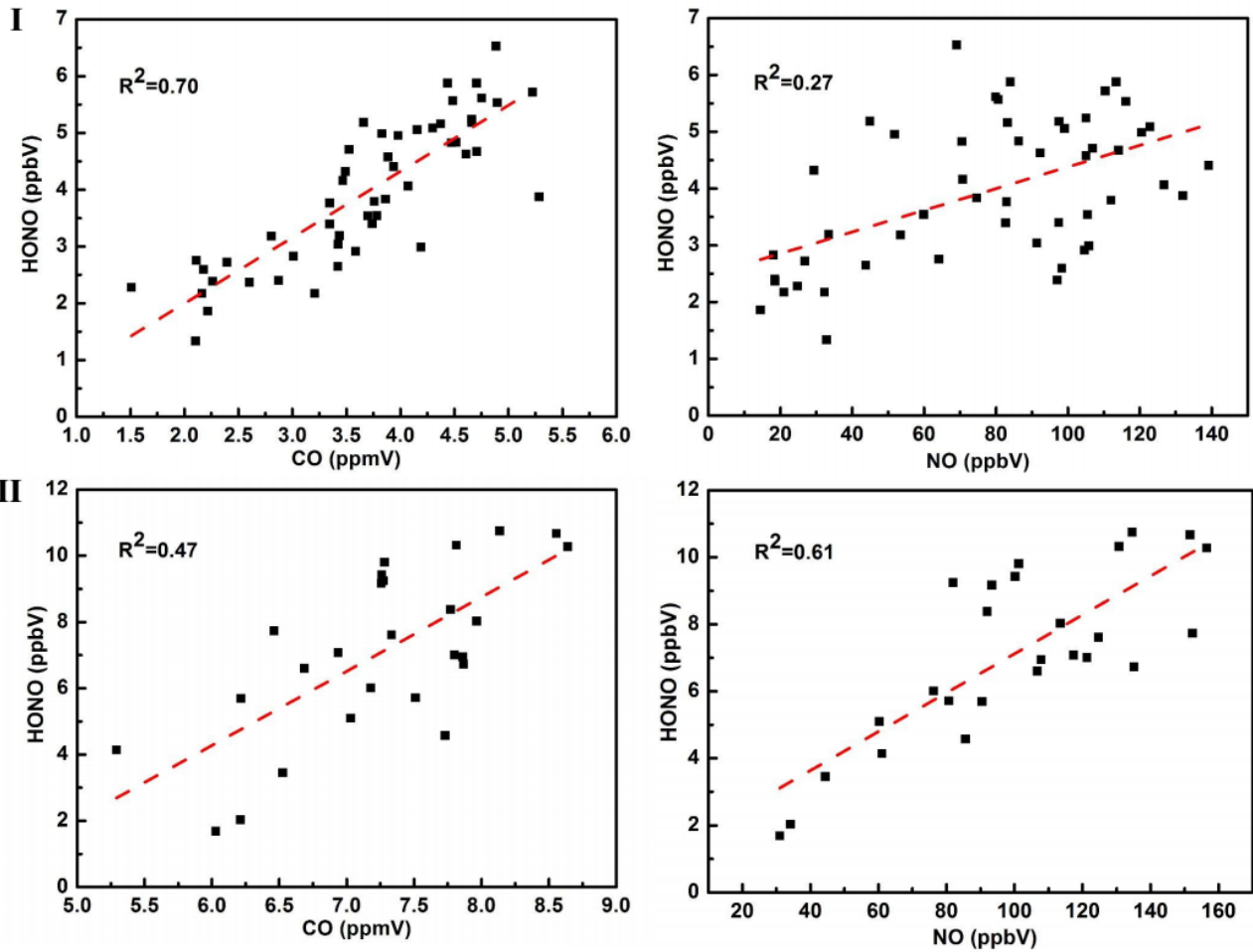
258 0.47 and 0.61 during periods I and II, respectively. It implied that the HONO sources were partly
 259 related to those of CO and NO at nighttime. Black carbon (BC) is another primary pollutant typically

260 emitted from combustion processes, such as diesel engines, industry, residential solid fuel, and open
 261 burning (Bond et al., 2013). The BC time series during periods I and II is shown in Fig. S3, BC was

262 generally higher during the nighttime than that during the daytime, with peaks at around midnight,
 263 resulting from burning coal for heating and diesel vehicles (allowed to enter Fifth Ring Road of

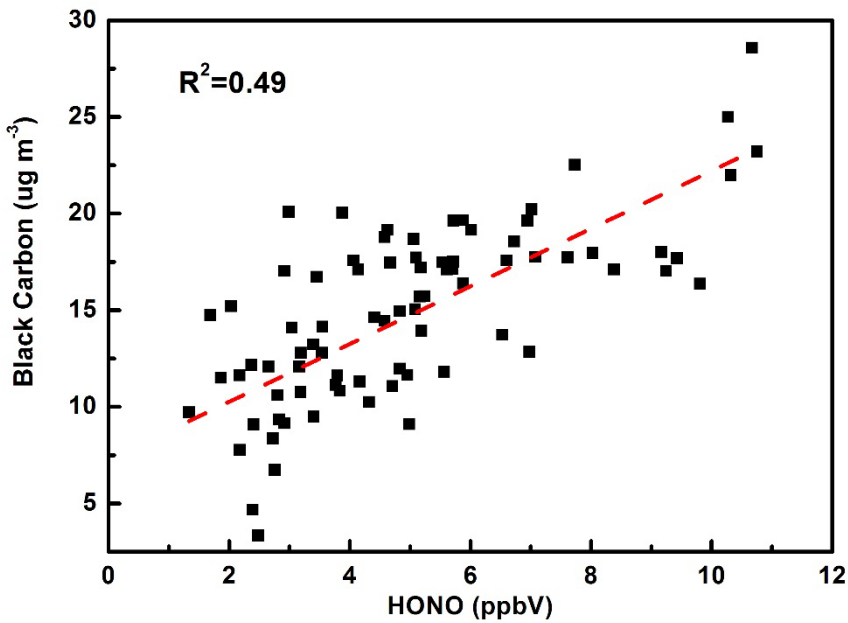
264 Beijing during 23:00 LT~ next 06:00 LT) emissions. The high correlation of HONO with BC ($R^2 =$
 265 0.49) (Fig. 8) also suggested a possible combustion HONO source, including vehicle emissions.

266 In urban areas, biomass burning is insignificant and vehicle emissions are important parts of direct
267 emissions (Tong et al., 2016; Nakashima et al., 2017; Ropkins et al., 2017). Hereby, the contribution
268 of vehicle emissions to measured HONO is estimated. The vehicle emissions are calculated by
269 $[\text{HONO}_{\text{emission}}] = [\text{NO}_x] \times K$, where $[\text{HONO}_{\text{emission}}]$ and $[\text{NO}_x]$ are the HONO mixing ratios emitted
270 from vehicle emissions and the observed NO_x mixing ratios, respectively. K is the emission factor.
271 During this haze episode (from 16 to 21 Dec.), the Beijing government issued an odd-even car ban
272 requiring alternate driving days for cars with even- and odd-numbered license plates. It means that
273 vehicle emissions might differ from normal. In order to determine the value of emission factor, we
274 used the nighttime HONO data and simultaneous NO_x mixing ratios greater than 20 ppbV (Su et al.,
275 2008). With the air aging, the HONO/ NO_x ratio gradually increased owing to the conversion of NO_2
276 to HONO, and thus we use the minimum HONO/ NO_x ratio during our measurement period, which is
277 1.3%, as the emission factor (Li et al., 2012). This is comparable to the result of 1.0% ($\pm 0.5\%$)
278 reported in Hong Kong by Yun et al. (2017) and in the range of 0.16% ~ 2.1% derived by previous
279 studies (Liu et al., 2017b; Trinh et al., 2017; Kurtenbach et al., 2001). Using this method, the
280 contributions of vehicle emissions to ambient HONO were estimated to be 52% ($\pm 16\%$) and 40% (\pm
281 18%) during periods I and II, respectively. Thus direct emissions from engine exhaust could be an
282 important source of HONO in Beijing.



283

284 **Fig. 7.** Correlations of HONO with CO and NO at nighttime during periods I and II.



285

286 **Fig. 8.** The correlation of HONO with BC at nighttime during periods I and II.

287 In summary, the secondary formation of HONO (homogeneous processes and heterogeneous
 288 conversion of NO₂) strengthened and primary emissions decreased from period I to period II.
 289 Although the heterogeneous conversion of NO₂ contributed to nocturnal HONO, it did not seem to
 290 be important. Direct emissions especially vehicle emissions were likely to be a more important
 291 source. Moreover, homogeneous processes could also played a noticeable role and should be
 292 reconsidered under high-NO_x conditions. In addition, the decrease in the boundary layer height may
 293 also contribute to nighttime HONO mixing ratios (Yu et al., 2009), especially before midnight. Thus
 294 more relative parameters and further studies are expected to explore the reasons for high levels of
 295 HONO at nighttime.

296 3.4. Daytime HONO budget

297 During periods I and II, the levels of NO maintained relatively high with a mean mixing ratio of 69
 298 ppbV, indicating that the homogeneous reaction might be significant during the daytime. To support
 299 this argument, daytime HONO formation rates during periods I and II can be calculated by the
 300 following equation (Soergel et al., 2011):

$$\begin{aligned}
 \frac{d\text{HONO}}{dt} &= \text{sources} - \text{losses} \\
 &= (P_{\text{OH+NO}} + P_{\text{other}}) - (L_{\text{OH+HONO}} + L_{\text{photo}} + L_{\text{dep}})
 \end{aligned}
 \tag{4}$$

302 Such that,

$$P_{\text{OH+NO}} + P_{\text{other}} = \frac{\Delta\text{HONO}}{\Delta t} + L_{\text{OH+HONO}} + L_{\text{photo}} + L_{\text{dep}}
 \tag{5}$$

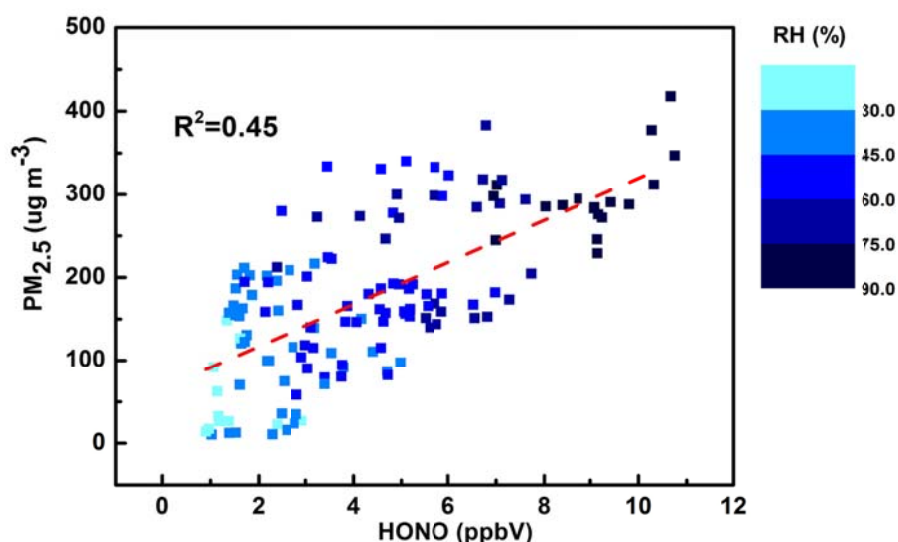
304 Where dHONO/dt represents the variation of measured HONO mixing ratios and can be substituted
 305 by ΔHONO/Δt. P_{OH+NO} and L_{OH+HONO} represent the homogeneous formation and loss rate of reaction
 306 R2 and R3, respectively. The expressions of P_{OH+NO} and L_{OH+HONO} have been discussed in section
 307 3.3.1. P_{other} represents other sources of measured HONO mixing ratios other than the homogeneous

308 reaction of NO with OH. L_{photo} is the HONO photolysis loss rate of reaction R1, which was
309 calculated by $L_{\text{photo}} = J_{\text{HONO}} \times [\text{HONO}]$, J_{HONO} is the photolysis frequency of HONO. L_{dep} represents
310 the dry deposition of HONO and is expressed by $L_{\text{dep}} = V_d \times [\text{HONO}] / H$, where V_d is the deposition
311 velocity of HONO and H is the daytime mixing height. V_d was 1.6 cm s^{-1} and H was assumed as 500
312 m according to previous studies (Hou et al., 2016; Li et al., 2011). Due to the values of OH radicals
313 and J_{HONO} were not available in this study, the NCAR Tropospheric Ultraviolet and Visible (TUV)
314 transfer model (http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/) and O_3 column density
315 measured by the Total Ozone Mapping Spectrometer (TOMS, data available at
316 <https://ozoneaq.gsfc.nasa.gov/data/ozone/>) were used (Huang et al., 2017; Spataro et al., 2013).
317 Considering the effects of aerosol on J values, aerosol optical parameters including aerosol optical
318 depth (AOD), single scattering albedo (SSA) and Angstrom exponent were set as inputs in the TUV
319 model. The typical AOD, SSA and Angstrom exponent values of 1.535, 0.88 and 1.4 were considered,
320 respectively, for the two haze periods I and II (Che et al., 2015; Hou et al., 2016; Jing et al., 2015;
321 Zhang et al., 2014). During the daytime (10:00 LT ~ 15:00 LT), the calculated J_{HONO} values varied
322 from 1.02×10^{-4} to $2.22 \times 10^{-4} \text{ s}^{-1}$, comparable to previous reports (Hou et al., 2016; Huang et al.,
323 2017). Based on the strong correlations of $J_{\text{O}^1\text{D}}$ (derived by TUV model) with OH radicals, the
324 simultaneous OH concentrations were calculated (Rohrer et al., 2006; Lu et al., 2013). The hourly
325 average OH ranged from 1.66×10^6 to $2.21 \times 10^6 \text{ cm}^{-3}$ from 10:00 LT to 15:00 LT during periods I
326 and II, within the range of observed OH in the northern parts of China by Lu et al. and Tan et al. (Lu
327 et al., 2013; Lu et al., 2012; Tan et al., 2017) and comparable to the study (observed OH
328 concentration at noontime of $2.4 \times 10^6 \text{ cm}^{-3}$ in severely polluted air from January to March) at a
329 suburban area of Beijing in winter 2016 by Tan et al. (2018).

330 The average production ($P_{\text{OH+NO}}$) and loss ($L_{\text{OH+HONO}}$, L_{dep} and L_{photo}) rates for daytime HONO
331 budget during periods I and II are illustrated in Fig. S4. The mean values of $L_{\text{OH+HONO}}$, L_{dep} and L_{photo}
332 were 0.07 ± 0.03 , 0.22 ± 0.12 and 1.15 ± 0.61 ppbV h⁻¹, respectively during period I, and 0.11 ± 0.06 ,
333 0.34 ± 0.21 and 1.84 ± 1.07 ppbV h⁻¹, respectively during period II. The average $P_{\text{OH+NO}}$ were $3.04 \pm$
334 1.72 and 3.43 ± 1.66 ppbV h⁻¹, during periods I and II respectively, which is much higher compared
335 to previous reports (Hou et al., 2016; Huang et al., 2017; Wang et al., 2017). Although the $P_{\text{OH+NO}}$ has
336 a large uncertainty, it played a key role in daytime HONO budget. And it was even enough to explain
337 the HONO sources during the daytime, if that is the case, there could be one or more important sinks
338 other than HONO photolysis, deposition of HONO and gas-phase reaction of HONO with OH to
339 mediate the discrepancy between sources and sinks of daytime HONO in such complicated pollution
340 periods.

341 3.5. The correlations between HONO, PM_{2.5} and RH

342 Fig. 9 illustrates the correlations between HONO, PM_{2.5} and the RH. PM_{2.5} increased with HONO
343 mixing ratios and RH, and had a pronounced correlation with HONO ($R^2 = 0.45$), suggesting a
344 potential chemical link between HONO and haze particles (An et al., 2013; Huang et al., 2014).
345 Moreover, increased RH is favorable for uptake and mass transport of reactive trace gases, such as
346 SO₂ and N₂O₅, which facilitated reactions of reactive trace gases into particles and accelerating
347 formations of secondary pollutants during heavy haze episodes (Liu et al., 2017a).



348

349 **Fig. 9.** Correlations between HONO, PM_{2.5} and RH during periods I and II.

350 4. Conclusions

351 Atmospheric nitrous acid (HONO) was measured during a severe pollution episode, in Beijing. The
 352 mean mixing ratio of HONO during the whole measurement was 3.5 ppbV with a maximum of 10.7
 353 ppbV. The HONO level was much higher than other observations in Beijing during recent years. The
 354 measurement was classified into haze (I), severe haze (II) and clean (III) periods. Vehicle emissions
 355 contributed 52% (± 16)% and 40% (± 18)% of the nighttime HONO during periods I and II,
 356 respectively and could be important HONO sources during this haze episode. Moreover, the
 357 heterogeneous conversion of NO₂ did not seem to be important at nighttime. The contribution of
 358 homogeneous reaction of NO with OH should be reconsidered and might be crucial under high-NO_x
 359 conditions. And poorer dispersion conditions may also contributed to high HONO mixing ratios
 360 during this haze event. More studies are required to accurately estimate not only HONO sources but
 361 also HONO sinks in the real atmosphere. In addition, an obvious correlation between HONO and
 362 PM_{2.5} indicated that HONO had a potential chemical link with haze particles.

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