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Atmospheric nitrous acid (HONO) in an alternate process of haze pollution and ozone pollution in urban Beijing in summertime: Variations, sources and contribution to atmospheric photochemistry

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1 1 **Atmospheric nitrous acid (HONO) in an alternate process of haze**
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3 2 **pollution and ozone pollution in urban Beijing in summertime:**
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6 3 **Variations, sources and contribution to atmospheric photochemistry**

7
8 4 Yunfeng Li^{1,2}, Xuezhong Wang¹, Zhenhai Wu¹, Ling Li³, Chuhan Wang¹, Hong Li^{1,*},
9 5 Xin Zhang^{1,2}, Yingnan Zhang², Junling Li¹, Rui Gao^{1,*}, Likun Xue²,
10 6 Abdelwahid Mellouki⁴, Yangang Ren⁴, Qingzhu Zhang²
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16

- 17 8 1. State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese
18 9 Research Academy of Environmental Sciences, Beijing 100012, China
19
20 10 2. Environment Research Institute, Shandong University, Qingdao 266237, China
21
22 11 3. Chongqing Research Academy of Eco-Environmental Sciences, Chongqing
23 12 401147, China
24
25 13 4. Institut de Combustion, Aérothermique, Réactivité et Environnement (ICARE),
26 14 CNRS (UPR 3021), Orléans 45071, France
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*Corresponding authors.

E-mail: lihong@craes.org.cn (Hong Li); gaorui@craes.org.cn (Rui Gao)

Abstract

Nitrous acid (HONO), as a key reservoir of hydroxyl radical (OH), plays a significant role in atmospheric chemistry. To study the sources and atmospheric influence of HONO, continuous observations of HONO and relevant air pollutants were performed from June to July 2019 at an urban site in Beijing. A comparative study on the ambient levels, diurnal variation, the sources in daytime and nighttime, and the formation mechanisms were investigated for a haze pollution period (Period I) and an ozone pollution period (Period II). The average hourly HONO concentrations during Period I, Period II, and the whole observation period, were 0.58 ± 0.23 , 0.54 ± 0.19 and 0.44 ± 0.24 ppb, respectively. The emission from vehicle exhaust was an important source of nocturnal HONO formation. During the nighttime, compared with the homogeneous reaction of NO with OH, the heterogeneous conversion from NO₂ was the dominant pathway for HONO formation. The heterogeneous conversion frequency was 0.0075 h^{-1} during Period I, higher than that during Period II (0.0028 h^{-1}), suggesting a higher conversion potential to HONO formation during the haze episode. Based on the analysis of HONO budget, it was found that the daytime unknown source P_{unknown} during Period II was higher than that during Period I. Correlation analysis implied that the photo-enhanced NO₂ conversion on the aerosol surface might be a potential source

1 53 for daytime HONO. Without HONO constraint, the Observation-Based Model (OBM)
2 54 would largely underestimate the averaged daytime atmospheric oxidative capacity
3
4 55 (24%), OH production rate (57%), and net O₃ production rate (20%). The study results
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6 56 further demonstrated the necessity for clarifying the formation mechanism of HONO
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8 57 to improve the understanding of the influence of HONO to atmospheric chemical
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10 58 processes.

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19 62 **Keywords:** Nitrous acid (HONO); Haze pollution period; Ozone pollution period;
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21 63 Heterogeneous conversion; unknown daytime source; Observation-Based Model;

22 64 **1. Introduction**

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26 65 Nitrous acid (HONO) is recognized as a significant precursor of the hydroxyl
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28 66 radical (OH), the dominant oxidant in the atmosphere (Kleffmann 2007; Su et al. 2011;
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30 67 Villena et al. 2011). OH radicals can further initiate atmospheric photochemistry
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32 68 leading to the formation of ozone (O₃) and secondary organic aerosols (SOA)
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34 69 (Hofzumahaus et al., 2009). Previous studies showed that HONO could only be the
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36 70 source of OH in the early morning (Winer and Biermann, 1994), however, it had been
37
38 71 found that HONO also contributed significantly (from 24% to 87%) to OH production
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40 72 during the entire daytime (Acker et al., 2006b; Czader et al., 2012; Fu et al., 2019;
41
42 73 Kleffmann et al., 2005; Li et al., 2018b; Ren et al., 2003; Su et al., 2008b; Yun et al.,
43
44 74 2017). Therefore, the better understanding of the variations, sources, and formation
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46 75 mechanisms of HONO is critical for obtaining more clear idea of the atmospheric
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48 76 oxidation processes.

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51 77 Many field measurements have been carried out at urban, rural, and remote sites
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53 78 in the world in the recent years, indicating that ambient HONO concentrations varied
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55 79 from several ppt in clean areas up to 15 ppb in polluted areas (Elshorbany et al., 2009;
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57 80 Jia et al., 2020; Kang et al., 2006; Liu et al., 2020; Nakashima et al., 2017; Shi et al.,
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59 81 2020; Spataro and Ianniello, 2014; Spataro et al., 2013; Villena et al., 2011; Xue et al.,
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1 82 2020; Yu et al., 2009b; Zhang et al., 2020; Zheng et al., 2020). Qin et al. (2009)
2 83 measured a nocturnal maximum HONO concentration of 8.4 ppb at an urban site in
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4 84 Guangzhou, with an unexpected high daytime concentration up to 2.0 ppb. In recent
5
6 85 years, Spataro et al. (2013) observed a high level of HONO up to 9.71 ppb in urban
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8 86 sites of Beijing. Fu et al. (2019) found that concentration of HONO reached 8 ppb in a
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10 87 severe haze pollution episode in the Pearl River Delta of China. During a biomass
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12 88 burning period, overall high HONO concentrations ranging from 0.01 ppb to 5.95 ppb
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14 89 were observed at a suburban site in Nanjing (Nie et al., 2015). Even in the remote Arctic
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16 90 area, HONO concentrations ranging between 0.04 and 37.9 ppt had been reported
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18 91 (Spataro et al., 2017). Generally, different levels of HONO were observed under
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20 92 different environmental conditions.
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22
23 93 As far as we know, the sources for atmospheric HONO are still not fully
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25 94 understood. The gas-phase reaction of NO and OH is once thought to be the only
26
27 95 predominant source of HONO during the daytime. However, such a mechanism could
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29 96 not explain the observed much higher daytime HONO concentrations, implying some
30
31 97 unknown sources existing. To explain the abnormal high daytime HONO, several
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33 98 sources of HONO have been proposed, including direct emissions from vehicle exhaust
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35 99 (Kurtenbach et al., 2001; Liu et al., 2017; Nakashima and Kajii, 2017), heterogeneous
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37 100 formation on wet surfaces (Han et al., 2016; Monge et al., 2010; Ren et al., 2020), soil
38
39 101 nitrite emission (Su et al., 2011; Yang et al., 2020), particulate nitrate photolysis (Shi et
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41 102 al., 2020; Yang et al., 2018a; Ye et al., 2016; Zhang et al., 2020; Zheng et al., 2020) and
42
43 103 conversion of nitric acid (Gall et al., 2016; Leong et al., 2016; Rutter et al., 2014;
44
45 104 Ziemba et al., 2010). And the well-accepted new HONO source is the heterogeneous
46
47 105 conversion of NO₂ on humid surfaces (Ma et al., 2017). The uptake coefficient (γ) relies
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49 106 on NO₂ concentrations and various parameters including types of surfaces, relative
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51 107 humidity, surface-to-volume ratio (S/V), and surface water content (Finlayson-Pitts et
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53 108 al., 2003; Stutz et al., 2004; Stutz et al., 2002). Liu et al. (2014) calculated that the γ
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55 109 value for aerosol uptake of NO₂ could reach up to $\sim 10^{-4}$ in the afternoon when HONO
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57 110 lifetime is the shortest due to the photolysis, suggesting the significant role of aerosols
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59 111 as reaction media.
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1 112 In the past 10 years, some studies have been carried out on the ambient levels and
2 113 formation mechanisms of HONO in China (Hendrick et al., 2014; Hou et al., 2016; Jia
3 114 et al., 2020; Liu et al., 2020; Liu et al., 2014; Meng et al., 2020; Spataro et al., 2013;
4 115 Wang et al., 2017; Yang et al., 2014; Zhang et al., 2019a; Zhang et al., 2019b; Zhang et
5 116 al., 2020). However, most studies focused on the characteristic and source of HONO
6 117 during the severe haze period, the HONO observations over the ozone pollution period
7 118 were limited in China. In this study, we performed the high time-resolved observation
8 119 of HONO in an urban site of Beijing in summer of 2019. In the following sections, we
9 120 first compared the atmospheric levels and variations of HONO and related species
10 121 during a haze pollution period and an ozone pollution period. Then, we explored several
11 122 sources of HONO in the two typical cases. Finally, the impacts of HONO on
12 123 atmospheric oxidative capacity (AOC), primary OH radical production, and O₃
13 124 production rates were assessed.

125 **2. Experimental**

126 **2.1 Site description**

127 The observation campaign was conducted from 13 June to 4 July 2019. The
128 observation site is on the roof (about 8 m above ground) of the Laboratory of
129 Atmospheric Photochemical Simulation of Chinese Research Academy of
130 Environmental Sciences (CRAES, 40.04° N, 116.42° E), in the north of Chaoyang
131 District of Beijing (Fig. S1). Chaoyang District is one of the six main urban districts
132 (Haidian, Chaoyang, Dongcheng, Xicheng, Shijingshan and Fengtai) of Beijing and is
133 located at the eastern area of Beijing. The CRAES site is to the north (about 2 km) of
134 the North Fifth Ring Road with high level of heavy traffic. It is located in a residential
135 and commercial area, without obvious industrial pollution sources nearby (Cheng et al.,
136 2018; Zhang et al., 2017). Thus, CRAES site could be considered as an urban site that
137 can represent the urban environment of Beijing.

139 **2.2 Measurements**

140 **2.2.1 HONO measurement**

141 HONO was measured by an online commercial long path absorption photometer
142 instrument (LOPAP-03, QUMA, Germany) by wet chemical sampling and photometric
143 detection. A detailed description of the HONO instrument has been described
144 previously (Li et al., 2012). Briefly, gaseous HONO are sampled by the absorption
145 solution (0.06 mol/L sulfanilamide in 0.1 mol/L HCl) in an external sampling unit. Then
146 the solution can react with 0.4 mmol/L N-(1-naphthyl) ethylenediamine-
147 dihydrochloride solution to generate a stable diazonium salt which can be detected
148 photo-metrically. The LOPAP is designed as a two-channel system to minimize
149 potential interferences (e.g. PAN and NO₂+SO₂) (Heland et al., 2001). In channel 1, all
150 HONO as well as the possible interferences are detected, while in channel 2 the same
151 amount of interferences without HONO are quantified. The absorption spectra are
152 recorded in 30 s intervals and the absorbance at 550 nm is used to evaluate the
153 concentration of HONO. The sampled airflow is set to 1000 ml/min. With the above
154 settings, the HONO sampling efficiency is determined to be near 100%. Calibration by
155 using the known nitrite standard solution was performed every three or four days
156 (Monday and Thursday) during the campaign. Zero measurements by sampling pure
157 nitrogen were conducted automatically every 8 hours. The detection limit of the
158 measurement is 4 ppt with an accuracy of 10%. The maximum detection limit is 2 ppm
159 and the observed HONO concentrations are within the range.

160 **2.2.2 Other measurements**

161 The NO, NO₂ and NO_x concentrations were measured by a chemiluminescence
162 instrument (Thermo 17i, USA) coupled with a molybdenum converter. It is noted that
163 NO₂ can be overestimated due to the potential conversion of other nitrogen-contained
164 species (e.g., peroxyacetyl nitrate (PAN)). However, Xu et al. (2013) have reported that
165 the overestimation was small at the urban sites affected by fresh emissions. Additionally,
166 the interference was also considered to be small because of the weak photochemical
167 reactions at night (Nie et al., 2015). The O₃ concentration was monitored by a UV
168 photometric O₃ analyzer (Thermo 49i, USA). CO was monitored by the infrared
169 absorption method using a CO analyzer (Thermo 48i, USA). Zero air was injected into
170 the CO analyzer to check zero drift every night and calibrate the analyzer once the zero

171 drift being bigger than 0.1ppm. The PM_{2.5} mass concentration was detected by the
172 model 5030 sharp PM_{2.5} monitor (Thermo, USA). Routine maintenance has been
173 carried out to ensure the accuracy of these data. The detection limits for Model 17i,
174 Model 49i, Model 48i, Model 5030 are 1.0 ppb, 1.0 ppb, 0.04 ppm, 0.5 µg/m³,
175 respectively.

176 The VOCs species were measured by an AirmoVOC online analyzer
177 (Chromatotec Group, Bordeaux, France) with the flame ionization detectors (FID).
178 Eighty-four VOCs species including 26 alkanes, 15 alkenes, 1 alkyne, 17 aromatic
179 hydrocarbons, and 25 halogenated hydrocarbons were detected with a time resolution
180 of 1 hour. Further detailed information could be found elsewhere (Cheng et al., 2018;
181 Zhang et al., 2017). The carbonyl compounds were collected into 2,4-
182 dinitrophenylhydrazine (DNPH) coated silica cartridges (Agela Technologies, China)
183 and analyzed by high-performance liquid chromatography (HPLC) based on the EPA
184 TO-11A method (USEPA, 1999). The detailed procedures of sampling and analytical
185 method can refer to our previous study (Zhang et al., 2019c). The carbonyl compounds
186 were measured from 22 to 26 June 2019, and the sampling resolution was two hours
187 during the campaign. Meteorological parameters consisting of wind speed (WS), wind
188 direction (WD), temperature (T), and relative humidity (RH) were measured by an
189 automatic weather station (MAWS301, Vaisala, Finland).

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191 **2.3 Model simulation**

192 **2.3.1 Observation-based Model**

193 An Observation-Based Model (OBM) incorporating the nearly explicit chemical
194 mechanism, Master Chemical Mechanisms (MCM, v3.3.1), has been widely employed
195 in previous studies to dissect the atmospheric oxidative capacity (AOC) and the
196 contributions of HONO to OH and O₃ production (Jiang et al., 2020; Xue et al., 2016;
197 Xue et al., 2014; Xue et al., 2013; Yang et al., 2018b; Yang et al., 2017). The MCM
198 described the detailed degradation reactions of 143 primary VOCs and the latest
199 inorganic reactions (Jenkin et al., 2003; Saunders et al., 2003). The heterogeneous
200 chemistry processes, dry deposition and dilution mixing within the boundary layer are

201 also included in the model. A more detailed description of this model configuration has
202 been provided elsewhere (Xue et al., 2016; Xue et al., 2014; Xue et al., 2013). The
203 model was constrained by the measured concentrations of O₃, SO₂, CO, NO, NO₂,
204 HONO, VOCs, carbonyls, J_{NO_2} , T, P and RH at a time resolution of 5 min. For VOCs
205 and carbonyl compounds, which were not measured in real-time, the time-dependent
206 data were linearly interpolated into 5 min. Such approximation may lead to some
207 uncertainties but should not significantly affect the estimation of the contribution of
208 HONO to OH production (Jiang et al., 2020; Yang et al., 2018b).

209 Here our emphasis is placed on the computation of AOC, OH production rates,
210 and O₃ budget. AOC is defined here as the sum of oxidation rates of VOCs and CO by
211 the dominant atmospheric oxidants including OH, O₃, and NO₃ (Xue et al., 2016). The
212 major primary sources of OH production include photolysis of O₃, HONO, and OVOCs
213 as well as reactions of O₃+VOCs (Jiang et al., 2020; Xue et al., 2016). The ozone
214 formation rates refer to the formation rates of the total oxidant (O_x=O₃+NO₂) instead
215 of O₃ alone (Xue et al., 2014; Xue et al., 2013). The situ O₃ photochemical formation
216 mechanism can be clarified into three pathways, HO₂+NO, CH₃O₂+NO, and other
217 RO₂+NO reactions. The O₃ loss pathways include NO₂+OH, RO₂+NO₂, O₃+OH/HO₂,
218 O₃ photolysis, and other reactions (VOCs+O₃, VOCs+NO₃, Heter.lossN₂O₅).
219 Considering the availability of carbonyls data, the model was only performed from 22
220 to 26 June (an ozone pollution period) with 00:00 local time (LT) as the initial time.
221 Two model cases with and without HONO constraints were run to assess the role of
222 HONO to AOC, OH production rate, and ozone budget. A six-day pre-run was made to
223 stabilize the unconstrained compounds and the final outputs were extracted to further
224 analyses.

225 **2.3.2 Photolysis rates and OH concentration**

226 The photolysis rates of HONO and O(¹D) were not measured directly in this work.
227 The J_{HONO} and $J_{\text{O}^1\text{D}}$ values can be calculated by the Tropospheric Ultraviolet and Visible
228 (TUV) radiation model developed by the Nation Center for Atmospheric Research
229 (NCAR) (<http://www.acd.ucar.edu/TUV>). To reflect the influence of aerosols on J_{HONO}
230 and $J_{\text{O}^1\text{D}}$ values, aerosol vertical optical depth (AOD), single scattering albedo (SSA),

1 231 and angstrom exponent values (α) were input into the TUV model. The AOD, α , O₃
2 232 column concentration, and cloud optical thickness were determined by Moderate
3
4 233 Resolution Imaging Spectroradiometer (MODIS) satellite
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6 234 (<https://neo.sci.gsfc.nasa.gov/blog/>). In our work, the value of 0.91 was used as SSA
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8 235 for the Beijing summer period (Spataro et al., 2013; Yu et al., 2009a).

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10 236 As OH concentration is not available in our study, the daytime OH concentration
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12 237 can be estimated by using the empirical power-law Eq. (1) (Rohrer and Berresheim,
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14 238 2006) below:

$$17 \quad 239 \quad \quad \quad [\text{OH}] = a \times (J_{\text{O}^1\text{D}}/10^{-5}\text{s}^{-1})^b + c \quad (1)$$
$$18 \quad 240 \quad \quad \quad (a = 4.2 \times 10^6 \text{ cm}^{-3}, b = 1.0, c = 0.6 \times 10^6 \text{ cm}^{-3})$$

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20
21 241 Where [OH] represents the OH concentration, $J_{\text{O}^1\text{D}}$ is the photolysis frequencies
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23 242 of O¹D modelled by the TUV model. The daytime OH concentration ranged from 6.5
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25 243 $\times 10^5$ to 9.2×10^6 molecule cm^{-3} with the mean value of 4.4×10^6 molecule cm^{-3} , which
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27 244 is within the range of those measured in Beijing (Lu et al., 2014; Tan et al., 2018). The
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29 245 correlations between the daytime calculated OH concentrations and the modelled
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31 246 concentrations by the OBM from 22 to 26 June were displayed in Fig. S2. The good
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33 247 correlations ($R^2=0.88$) showed the reliability of the OH concentrations calculated by
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35 248 the empirical power-law equation.

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40 250 **3. Results and discussion**

41 251 **3.1 Overview of measurements**

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44 252 The time series of HONO, O₃, CO, NO, NO₂, PM_{2.5} and meteorological parameters
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46 253 from 13 June to 4 July are displayed in Fig. 1. During the observation period, the
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48 254 temperature ranged from 18 to 38°C, with average values of 28 ± 4 °C; the RH ranged
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50 255 from 16% to 92%, with average values of 52 ± 18 %. The wind direction during the
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52 256 observation period was dominated by the south wind and the average WS was
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54 257 2.73 ± 1.65 m/s. Occasionally on 29 and 30 June, the dominant wind direction was north,
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56 258 and the hourly WS exceeded 7 m/s.

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58
59 259 The average hourly levels of NO, NO₂, and CO were 2.7 ± 1.9 ppb (1.0-14.2 ppb),
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1 260 15.5±8.8 ppb (1.7-54.5 ppb), and 1.20±0.32 ppm (0.47-2.57 ppm), respectively. The
2 261 levels of PM_{2.5} and O₃ ranged from 5.5 to 125.1 µg/m³ and from 1.0 to 157.7 ppb, and
3 262 averaged at 41.6±26.8 µg/m³ and 61.3±35.4 ppb, respectively. The measured hourly
4 263 concentrations of HONO ranged from 0.10 to 1.39 ppb, with an average of 0.44±0.24
5 264 ppb. The highest HONO concentration in the present study was comparable to the level
6 265 reported in a northwestern urban area of Beijing (Wang et al., 2017), but lower than the
7 266 levels in other urban areas in China, such as Beijing (3.24 ppb, (Hou et al., 2016); 3.69
8 267 ppb, (Spataro et al., 2013)), Xi'an (4.3 ppb, (Huang et al., 2017)), Shanghai (5.84 ppb,
9 268 (Cui et al., 2018)), and Hong Kong (13.9 ppb, (Yun et al., 2017)).

10 269 Based on the National Ambient Air Quality Standard (NAAQS) (GB 3095-2012),
11 270 only a haze day (19 June) occurred with daily PM_{2.5} concentrations exceeding the Grade
12 271 II of NAAQS (75 µg/m³). Seventeen O₃ non-attainment days (except 14, 16, 29-30 June
13 272 and 1 July) occurred with daily maximum-8h average concentrations exceeding the
14 273 Grade II of NAAQS (75 ppb, corresponding to 160 µg/m³). In this study, a haze
15 274 pollution period from 17 to 21 June (Period I, the blue area in Fig. 1) and an ozone
16 275 pollution period from 22 to 26 June (Period II, the orange area in Fig. 1) were selected
17 276 as two typical case studies. Table 1 documented the average hourly HONO, NO₂, NO,
18 277 PM_{2.5}, O₃ concentrations, and HONO/NO₂ ratio during the two periods. Given that the
19 278 NO_x analyzer probably overestimated the NO₂ concentrations, the HONO/NO₂ ratios
20 279 discussed in Section 3 are lower limits for the values. The average hourly HONO level
21 280 during Period I (*p*<0.05) was higher than that during Period II. The result of higher
22 281 HONO level during Period I was consistent with the previous studies (Cui et al., 2018;
23 282 Zhang et al., 2019b). The average hourly ozone levels were similar in two periods.
24 283 Compared with that during Period II, a higher HONO/NO₂ ratio was found during
25 284 Period I. The HONO/NO₂ ratio was often applied to assess the contribution of NO₂ to
26 285 HONO from the heterogeneous conversion (Li et al., 2012). It implied that the
27 286 heterogeneous conversion from NO₂ might contribute to HONO formation.

28 287 The averaged daytime and nighttime HONO, NO₂ and HONO/NO₂ of our
29 288 observation and other urban sites were summarized in Table S1. The higher HONO,
30 289 NO₂, and HONO/NO₂ levels occurred at nighttime in all sites except Nanjing (Liu et

1 290 al., 2019) and Hong Kong (Xu et al., 2015). The average nighttime HONO/NO₂ ratios
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3 291 obtained by this study were lower than those in previous results of Beijing (Jia et al.,
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5 292 2020; Tong et al., 2015), but comparable to measurements at Shanghai (Bernard et al.,
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7 293 2016), Hong Kong (Xu et al., 2015), Roma (Acker et al., 2006a), and Paris (Michoud
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9 294 et al., 2014). The lower HONO/NO₂ ratios may suggest a less conversion from NO₂ to
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11 295 HONO formation in this study.
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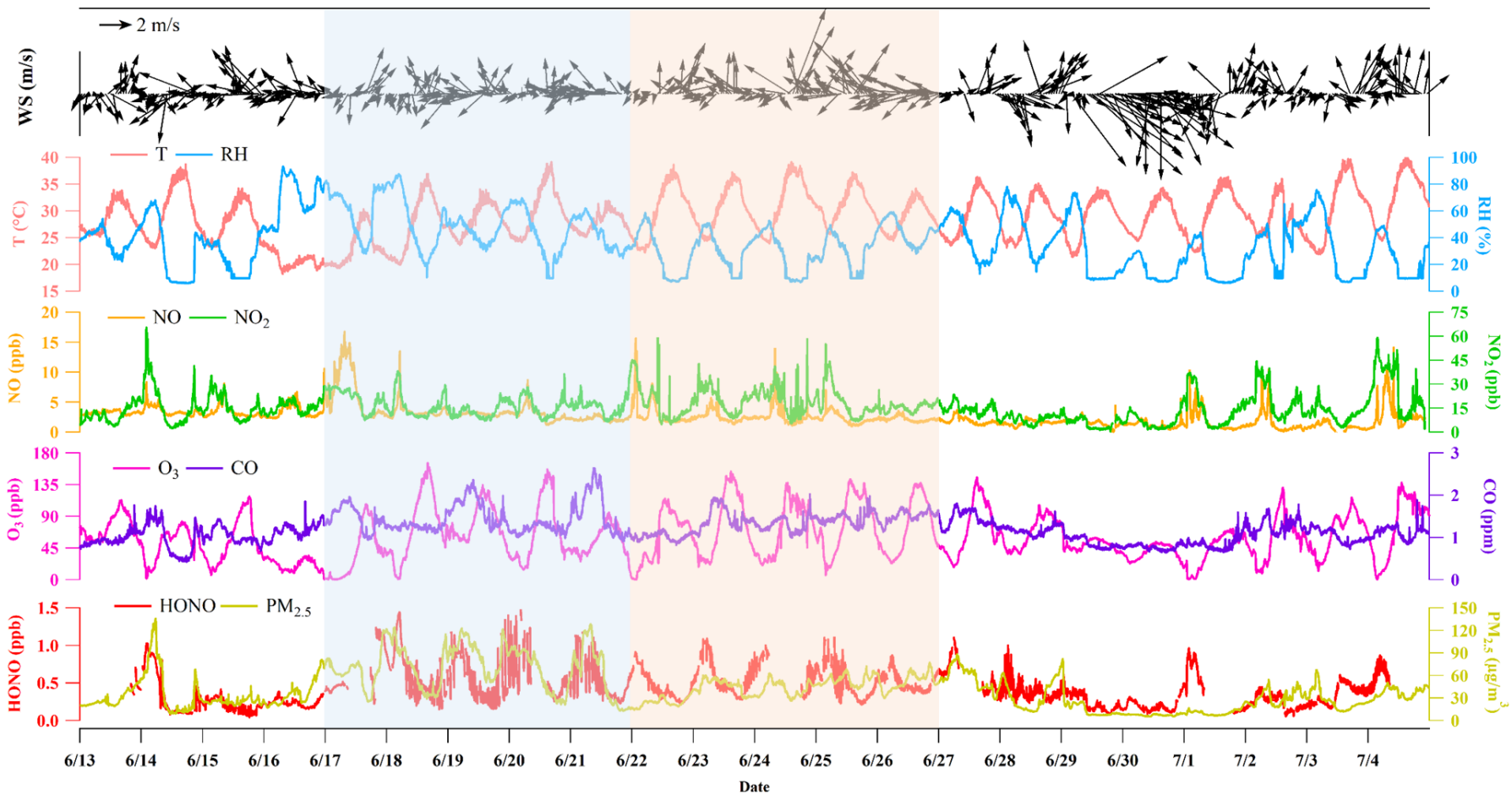


Fig. 1 Time series of HONO, O₃, CO, NO, NO₂, PM_{2.5}, and meteorological parameters from 13 June to 4 July 2019. Blue and orange areas are Period I (haze pollution) and II (ozone pollution), respectively. (Missing data are due to instrument maintenance)

299 **Table 1** Average hourly HONO, NO₂, NO, PM_{2.5}, O₃ concentrations, and HONO/NO₂
 300 ratios during the haze pollution period and the ozone pollution period

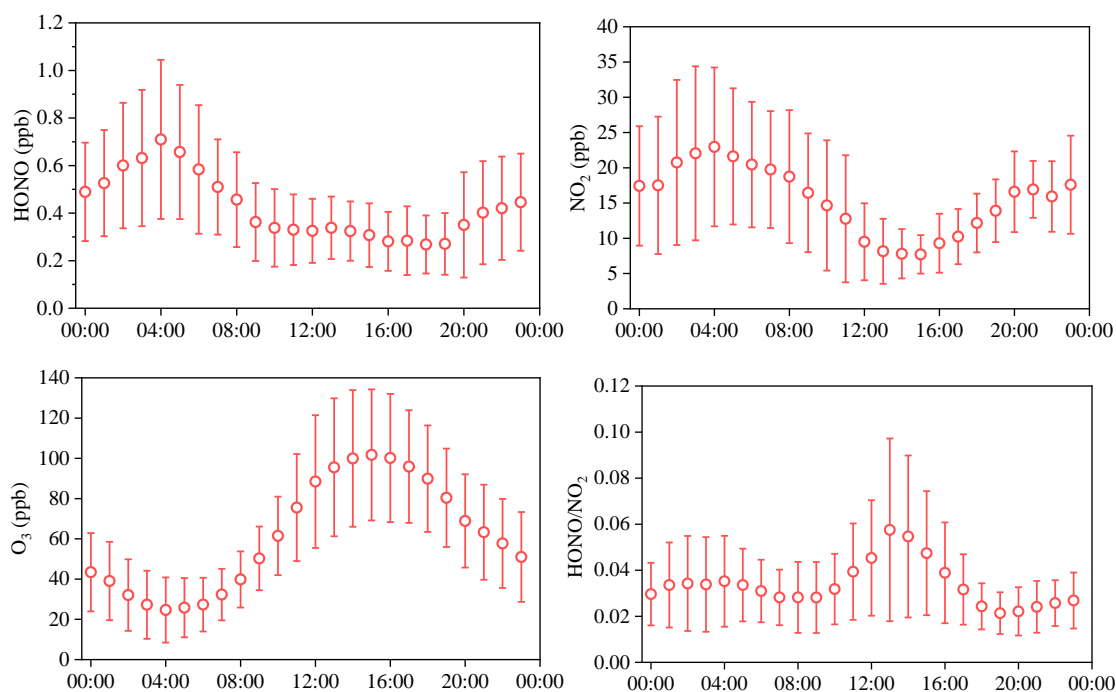
Pollutant	Unit	Period I	Period II
		Haze pollution period	Ozone pollution period
HONO	ppb	0.58±0.26 (0.25-1.39)	0.54±0.19 (0.24-1.04)
NO ₂	ppb	16.4±6.5 (7.4-38.7)	18.5±8.0 (6.1-44.0)
NO	ppb	3.6±2.5 (1.3-14.2)	2.6±1.5 (1.2-11.4)
PM _{2.5}	µg/m ³	69.5±29.7 (13.6-123.3)	43.5±13.4 (15.0-72.9)
O ₃	ppb	62.9±39.4 (1.0-157.7)	73.2±43.4 (1.0-145.0)
HONO/NO ₂	%	3.8±1.6 (1.4-9.2)	3.1±0.9 (1.4-5.8)

301

302 3.2 Diurnal variations of HONO

303 The diurnal profiles of HONO, NO₂, O₃, and HONO/NO₂ ratio were illustrated in
 304 Fig. 2. The obvious diurnal variation of HONO resembled those at other urban sites in
 305 previous studies (Huang et al., 2017; Li et al., 2018a; Michoud et al., 2014; Wang et al.,
 306 2017). After sunrise, HONO concentration dropped rapidly to ~0.33 ppb at noon due to
 307 photolysis and the elevated height of the boundary layer, the concentration of which
 308 remained at a low level until sunset. Then HONO concentration increased and
 309 accumulated during the night, reaching the peak value of 0.71 ppb at 04:00 LT. The
 310 diurnal cycle of NO₂ was similar to that of HONO. After sunset, NO₂ increased and
 311 maintained at a high level during the night. A maximum value of 23.0 ppb was also
 312 obtained at 04:00 LT. The diurnal cycle of O₃ was opposite to HONO and NO₂, with a
 313 maximum value of 101.7 ppb at 15:00 LT and a minimum value of 24.6 ppb at 04:00
 314 LT. The HONO/NO₂ ratio started to increase gradually after sunset and reached the first
 315 weak peak during the night (04:00 LT). The ratio had a second rising process after 09:00
 316 LT and climbed to the maximum at 13:00 LT. The values of HONO/NO₂ at noon (11:00-
 317 16:00 LT) were even higher than those during the night. If the sources of HONO were
 318 the same during the night and day, a low HONO/NO₂ ratio should be obtained at noon
 319 because of the strong photolysis of HONO. Thus, we can conclude the existence of an

320 additional source of HONO during the daytime, and further discuss the potential
321 daytime source of HONO in Section 3.4.



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323
324 **Fig. 2** Diurnal profiles of HONO, NO₂, O₃, and HONO/NO₂ ratio

325 (error bar means standard deviation)

326 327 3.3 Nocturnal HONO sources

328 3.3.1 Direct vehicle emission

329 Previous studies have shown that HONO can be directly emitted into the
330 atmosphere by combustion processes including vehicle exhaust and biomass burning
331 (Burling et al., 2010; Spataro and Ianniello, 2014). As our sampling site is close to the
332 five-ring road with high traffic volume, it is essential to assess the contribution of
333 vehicle emission to ambient HONO concentrations. The HONO/NO_x ratio was usually
334 used to derive the emission factor of HONO in the freshly emitted air masses
335 (Kurtenbach et al., 2001). A criterion of NO/NO_x > 0.7 was often adopted to select the
336 fresh air masses. However, in our study the relatively low NO/NO_x ratio (from 0.09 to
337 0.53) suggested that the air mass had become aged before arriving at the sampling site.
338 The HONO/NO_x ratios of 0.0065 (Spataro et al., 2013; Tong et al., 2015) and 0.008
339 (Jia et al., 2020; Meng et al., 2020; Zhang et al., 2020) have been chosen as the emission

340 factor for the urban area of Beijing in previous studies. Based on the tunnel studies
 341 (Kleffmann et al., 2003; Kurtenbach et al., 2001), the ratios ranging from 0.3% to 0.8%
 342 in fresh vehicle exhaust had been reported. Thus, the values of 0.003, 0.0065 and 0.008
 343 were adopted to estimate the contribution from traffic emission. The directly emitted
 344 HONO concentration can be calculated by Eq. (2) below:

$$345 \quad [\text{HONO}]_{\text{emis}} = [\text{NOx}] \times F \quad (2)$$

346 where, $[\text{HONO}]_{\text{emis}}$ represents the HONO levels from the traffic emission, $[\text{NOx}]$
 347 represents the NOx concentration, and F represents the emission factor. To avoid the
 348 influence of HONO photolysis, only the nocturnal data from 20:00 LT to the next 06:00
 349 LT were considered. The statistical results of the ratios of $[\text{HONO}]_{\text{emis}}/[\text{HONO}]$ were
 350 shown in Fig. S3. The average calculated $[\text{HONO}]_{\text{emis}}$ levels contributed 15%, 31%,
 351 and 40% to the whole measured nocturnal HONO levels at the emission factor of 0.003,
 352 0.0065 and 0.008, respectively. In previous studies, the contributions from vehicle
 353 emission ranged between 20.59% and 52% in urban areas of Beijing (Spataro et al.,
 354 2013; Tong et al., 2015; Zhang et al., 2019b). Therefore, direct emissions from vehicles
 355 could be an important HONO source in Beijing.

356 3.3.2 NO+OH homogeneous formation

357 The reaction of NO with OH was also anticipated as a dominant homogeneous
 358 production of HONO in nighttime (Li et al., 2012; Lu et al., 2014). Considering the
 359 reactions of R1 and R2, the net homogeneous HONO production ($P^{\text{net}}_{\text{OH+NO}}$) can be
 360 calculated by the following Eq. (3):

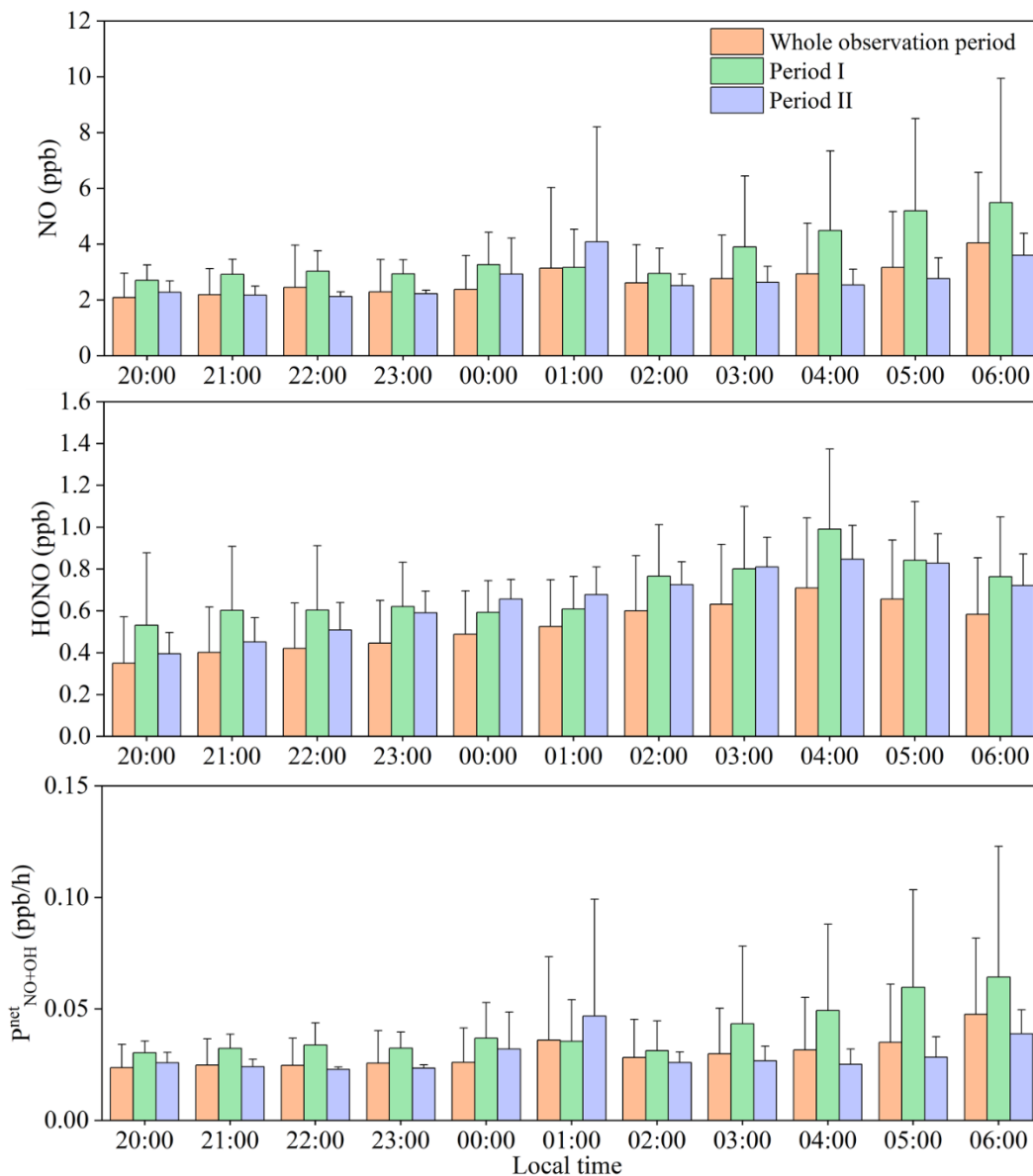


$$363 \quad P^{\text{net}}_{\text{NO+OH}} = k_{\text{NO+OH}}[\text{OH}][\text{NO}] - k_{\text{HONO+OH}}[\text{HONO}][\text{OH}] \quad (3)$$

364 where the rate constants $k_{\text{NO+OH}}$ and $k_{\text{HONO+OH}}$ are 7.2×10^{-12} and 5.0×10^{-12} cm^3
 365 $\text{molecule}^{-1} \text{s}^{-1}$ for reactions R1 and R2 at 298 K, respectively (Li et al., 2012); $[\text{NO}]$ and
 366 $[\text{HONO}]$ represents concentrations of NO and HONO, respectively. Since the rate
 367 constants of R1 and R2 are similar, the $P^{\text{net}}_{\text{NO+OH}}$ is determined by NO and HONO
 368 concentrations. The nighttime OH concentration with 5×10^5 molecules cm^{-3} was

369 observed by Tan et al. (2017) in Wangdu in summer 2014. An average value of $5.0 \times$
 370 10^5 molecules cm^{-3} was assumed to the nighttime OH concentration of Beijing in this
 371 study (Cui et al., 2018; Huang et al., 2017; Spataro et al., 2013; Tong et al., 2015).

372



373

374 **Fig. 3** Average nocturnal variations of $P^{\text{net}}_{\text{NO+OH}}$ during the whole observation period,
 375 Period I, and Period II (error bar means standard deviation)

376

377 Fig. 3 depicted the nocturnal variations of NO, HONO, and $P^{\text{net}}_{\text{NO+OH}}$ during the
 378 whole observation period, Period I, and Period II. Before midnight (20:00-00:00), the
 379 relatively low NO and HONO concentrations provided the low $P^{\text{net}}_{\text{NO+OH}}$ values of

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1 380 0.03±0.01 ppb h⁻¹ during the three periods. After midnight (01:00-06:00), the P^{net}_{NO+OH}
2 381 values during the three periods showed increase trends due to the increases of NO and
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4 382 HONO concentrations, averaged at 0.03±0.03, 0.05±0.03 and 0.03±0.01 ppb h⁻¹,
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6 383 respectively. Note that the P^{net}_{NO+OH} value averaged at 0.04±0.02 ppb h⁻¹ during Period
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8 384 I were slightly higher than those during the whole observation period (0.03±0.02 ppb
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10 385 h⁻¹) and Period II (0.03±0.01 ppb h⁻¹). The calculated average P^{net}_{NO+OH} ranged from
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12 386 0.002 to 0.17 ppb h⁻¹, which was comparable to those obtained at an urban site of
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14 387 Western China in summer (0.04-0.15 ppb h⁻¹) (Huang et al., 2017), but lower than the
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16 388 results in severe haze periods in urban Beijing (0.98-2.18 ppb h⁻¹) (Tong et al., 2015;
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18 389 Zhang et al., 2019b).

20 390 **3.3.3 Heterogeneous conversion of NO₂**

21 391 Numerous field measurements in urban sites reported that heterogeneous
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23 392 conversion reaction of NO₂ on wet surfaces could be an important HONO source at
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25 393 night in the atmosphere (Sorgel et al., 2011; Spataro et al., 2013; Su et al., 2008a). The
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27 394 NO₂ conversion efficiency mainly depends on the surface properties. The positive
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29 395 correlation between HONO and NO₂ (R²=0.31, shown in Fig. S4) was also found in
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31 396 this study, implying that NO₂ might be a precursor of HONO production (Huang et al.,
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33 397 2017; Qin et al., 2009).

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35 398 The aerosol surface is considered as an important media for the heterogeneous
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37 399 conversions of NO₂ in several studies (Huang et al., 2017; Li et al., 2012; Liu et al.,
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39 400 2014). As aerosol surface density is not measured, PM_{2.5} concentrations are used as
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41 401 surrogates to identify the influences of aerosols on HONO formation. Fig. 4(a) showed
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43 402 the correlation of HONO/NO₂ with PM_{2.5} concentrations at night, and the positive
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45 403 correlation revealed the heterogeneous conversions of NO₂ on aerosol surfaces.
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47 404 Additionally, it can be seen that the mean HONO/NO₂ value increased gradually with
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49 405 the increasing PM_{2.5} concentrations. The correlations between HONO/NO₂ and PM_{2.5}
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51 406 concentrations at night during Period I and Period II were displayed in Fig. S5. A higher
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53 407 correlation was found in Period I, indicating the possibility of a higher conversion
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55 408 frequency on aerosol surfaces in the haze pollution period than in the clean period.

56 409 The effects of RH on the heterogeneous formation of HONO are further

410 investigated. Stutz et al. (2004) asserted that the absorbed water on the surface
 411 participated in the heterogeneous conversion of NO₂ to HONO. The influence of RH
 412 on heterogeneous HONO formation at night was illustrated in Fig. 4(b). An increase of
 413 HONO/NO₂ along with the increasing RH was found when the RH was less than 60%.
 414 Further increase (>60%) of RH led to a decrease of the HONO/NO₂ value. This
 415 phenomenon can be associated with the number of water layers formed on aerosol
 416 surfaces. The excess water on the surface is a limiting factor for the NO₂ conversion.
 417 When the RH is larger than 60% in this study, the heterogeneous conversion efficiency
 418 seems to be depended negatively on RH. The similar phenomenon was also observed
 419 by Yu et al. (2009b) in Nepal, Li et al. (2012) and Wang et al. (2013) in China.
 420 Additionally, the water uptake processes could occur on aerosol/ground surfaces. Many
 421 studies have reported that the water droplets act as a role in the HONO sink when the
 422 RH exceeds 96% (Acker et al., 2005; He et al., 2006; Yu et al., 2009b; Zhou et al., 2007).
 423 Since the maximum RH is 92% in this study, the process of HONO uptake by water is
 424 not considered.

425 The conversion frequency (C_{HONO}) is widely used to estimate the conversion rate
 426 from NO₂. It was assumed that all measured HONO came from heterogeneous
 427 conversions of NO₂ (Hou et al., 2016), and the C_{HONO} value could be calculated by Eqs.
 428 (4) and (5) (Su et al. 2008a; Wang et al. 2017a; Zhang et al. 2019b). To eliminate the
 429 influence of direct vehicle emission, the HONO concentration was corrected by Eq. (6)
 430 and was denoted as $[HONO]_{corr}$.

$$\begin{aligned}
 431 \quad C_{HONO}^X &= \frac{2\left(\frac{[HONO_{corr}]_{t2} \times [\bar{X}] - [HONO_{corr}]_{t1} \times [\bar{X}]}{[X]_{t2}}\right)}{(t_2 - t_1) \left(\frac{[NO_2]_{t2} \times [\bar{X}] + [NO_2]_{t1} \times [\bar{X}]}{[X]_{t2}} + \frac{[NO_2]_{t1} \times [\bar{X}]}{[X]_{t1}}\right)} \\
 432 \quad &= \frac{2\left(\frac{[HONO_{corr}]_{t2} - [HONO_{corr}]_{t1}}{[X]_{t2}}\right)}{(t_2 - t_1) \left(\frac{[NO_2]_{t2} + [NO_2]_{t1}}{[X]_{t2}} + \frac{[NO_2]_{t1}}{[X]_{t1}}\right)} \quad (4)
 \end{aligned}$$

$$433 \quad C_{HONO} = \frac{1}{3} (C_{HONO}^0 + C_{HONO}^{CO} + C_{HONO}^{NO_2}) \quad (5)$$

$$434 \quad [HONO]_{corr} = [HONO] - [HONO]_{emis} \quad (6)$$

435 where $[HONO_{corr}]_t$, $[NO_2]_t$ and $[X]_t$ represents the concentrations of the HONO_{corr}, NO₂
 436 and reference gases at the time t, respectively. $[\bar{X}]$ is the averaged reference gases

437 concentration during the time interval of t_1 and t_2 . C_{HONO}^X is the conversion frequency
 438 scaled with reference gases X (CO and NO₂) and C_{HONO}^0 is the conversion frequency
 439 which is not scaled. The emission factor is 0.0065. The heterogeneous conversion rates
 440 of NO₂ were 0.0036 h⁻¹, 0.0075 h⁻¹, and 0.0028 h⁻¹ on average during the whole
 441 observation period, Period I and Period II, respectively. The rates were comparable to
 442 the values of 0.0039 h⁻¹ in winter of Beijing in 2014 (Hou et al., 2016), 0.0058 h⁻¹ in
 443 winter of 2016 (Zhang et al., 2019b), and 0.0078 h⁻¹ in autumn of 2018 (Jia et al., 2020),
 444 but lower than the values obtained in other studies of Beijing, such as 0.010 h⁻¹ in
 445 summer of 2016 (Wang et al., 2017) and 0.016 h⁻¹ in spring of 2018 (Zhang et al., 2020).
 446 Based on the study of Su et al. (2008a), the conversion rates could be affected by several
 447 factors including surface features, aerosol concentrations, and the environments. The
 448 discrepancies may be related to the different types of surface and aerosol concentrations
 449 in different environments. A heterogeneous production rate of HONO at night (C_{HONO}
 450 \times [NO₂]) of 0.06 ppb h⁻¹ was derived during the whole observation period, which is
 451 higher than the rate from homogeneous reaction of NO with OH. This showed that the
 452 heterogeneous conversion from NO₂ was more important for HONO formation at night
 453 during the observation period.

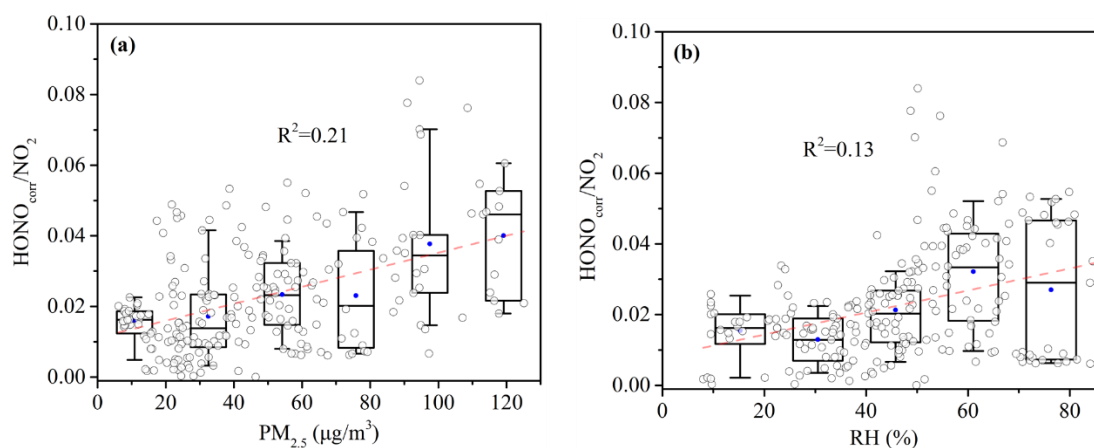


Fig. 4 The correlations between HONO_{corr}/NO₂ and PM_{2.5} concentration (a) and RH
 (b) at night. Mean (blue circle), median (middle horizontal line), 25th and 75th
 percentiles (P25-P75, box), 10th and 90th percentiles (P10-P90, whiskers).

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2 3 4 461 **3.4 Daytime HONO budget**

5 462 Several studies reported that the gas phase reaction of OH and NO was not
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7 463 sufficient to explain the HONO concentration in the daytime. An unknown daytime
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9 464 HONO source needs to be identified. Based on the source and sink pathways of HONO,
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11 465 the net daytime HONO formation rate can be calculated by a detailed budget Eq. (7)-
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13 466 (9) (Jia et al., 2020; Sorgel et al., 2011).

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$$\frac{d[HONO]}{dt} = P_{emis} + P_{OH+NO} + P_{unknown} - L_{HONO+OH} - L_{pho} - L_{dep} \quad (7)$$

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18 468
$$L_{pho} = J_{HONO} \times [HONO] \quad (8)$$

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20 469
$$L_{dep} = V_d \times [HONO] / H \quad (9)$$

21
22 470 where, $d[HONO]/dt$ means the variation of the observed HONO concentrations; P_{emis} ,
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24 471 P_{OH+NO} , and $P_{unknown}$ represent the contribution rates of direct vehicle emission, the
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26 472 homogeneous reaction of OH and NO and the unknown source, respectively. $L_{HONO+OH}$,
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28 473 L_{pho} , and L_{dep} donate the loss rate of the reaction of HONO with OH, the photolysis
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30 474 reaction of HONO, and the dry deposition of HONO, respectively. J_{HONO} is the
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32 475 photolysis frequency of HONO obtained by the TUV model simulation, varying from
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34 476 3.69×10^{-4} to $5.13 \times 10^{-4} \text{ s}^{-1}$ during the daytime (10:00 LT-15:00 LT). According to
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36 477 previous studies (Hou et al., 2016; Li et al., 2011), the deposition velocity V_d and the
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38 478 daytime mixing height H in Beijing were assumed as 1.6 cm s^{-1} and 500 m, respectively.

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41 479 Table 2 summarized the daytime HONO production rate from unknown source at
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43 480 different sites. The calculated average $P_{unknown}$ was 0.59 ppb h^{-1} (ranging from 0.02 to
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45 481 1.83 ppb h^{-1}) in our study, which was lower than those values in most urban sites, but
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47 482 comparable to the values (0.40 and 0.50 ppb h^{-1}) in sites of Paris and Germany.
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49 483 Interestingly, a larger $P_{unknown}$ (0.80 ppb h^{-1}) was found during Period II than the value
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51 484 (0.73 ppb h^{-1}) calculated during Period I. The diurnal contributions of production and
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53 485 loss pathways to the HONO budget during the whole observation period, Period I, and
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55 486 Period II were illustrated in Fig. 5, Fig. S6(a), and Fig. S6(b), respectively. The $P_{unknown}$
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57 487 values are still about 5-6 times greater than the P_{OH+NO} values, suggesting that $P_{unknown}$
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59 488 is the dominant daytime HONO source during the observation period. As the largest
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489 production process, the unknown source could account for up to 87% of the HONO
 490 production. The proportion could even reach up to 92% during Period II.

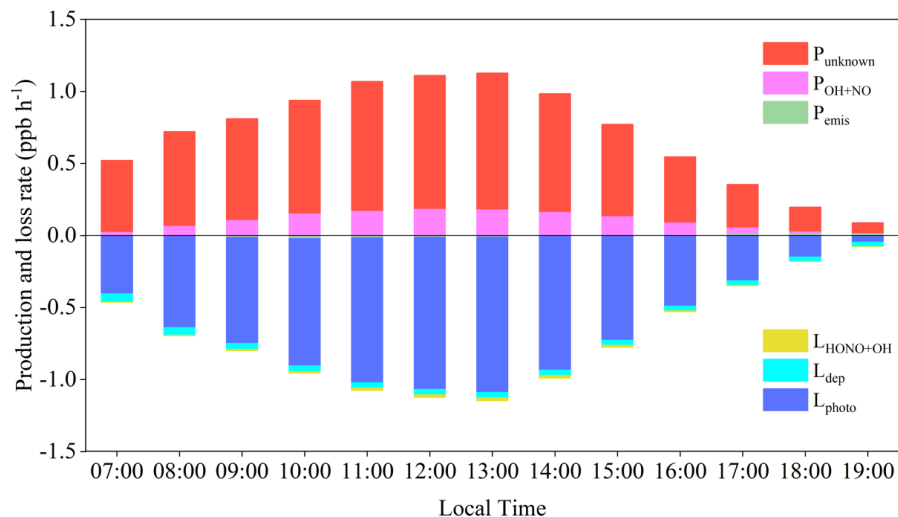
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Table 2 Comparison of the HONO concentrations and the derived P_{unknown} at different sites

Site	Date	HONO/ppb	$P_{\text{unknown}}/\text{ppb h}^{-1}$	Reference
Beijing (suburban, China)	2006.8	0.45	1.00	(Yang et al., 2014)
Beijing (urban, China)	2014.2-3	1.95	1.26-1.85	(Hou et al., 2016)
Beijing (urban, China)	2015.9- 2016.7	5.97	3.05	(Wang et al., 2017)
Beijing (urban, China)	2016.12	3.5	0.98-1.25	(Zhang et al., 2019b)
Beijing (urban, China)	2018.8-9	1.23	2.33	(Jia et al., 2020)
Beijing (urban, China)	2019.6-7	0.44	0.59	This study
Jinan (urban, China)	2015.9- 2016.8	1.15	2.95	(Li et al., 2018a)
Xi'an (urban, China)	2015.7-8	1.04	0.75	(Huang et al., 2017)
Shanghai (urban, China)	2016.5	2.31	1.78-2.98	(Cui et al., 2018)
Guangzhou (rural, China)	2004.10	1.25	4.90	(Su et al., 2008b)
Paris (suburban, France)	2009.7	0.10	0.40	(Michoud et al., 2014)
Jülich (rural, Germany)	2003.7-8	0.14	0.50	(Kleffmann et al., 2005)

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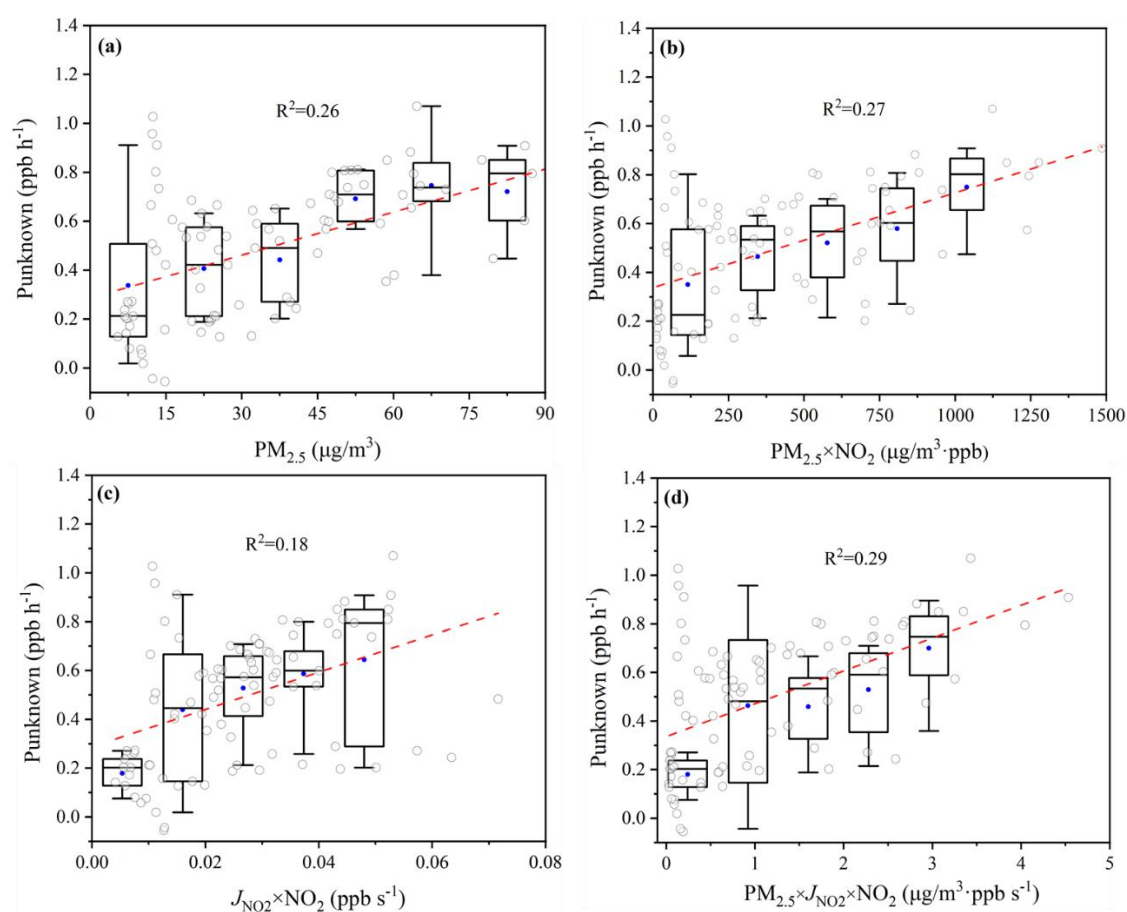


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495 **Fig. 5** Diurnal production and loss rates for the daytime HONO budget

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497 Understanding the potential unknown daytime sources of HONO is a challenging
498 task. Of note, as shown in Fig. 5, P_{unknown} climbed to the maximum at noon (13:00 LT)
499 and then gradually decreased. It could be inferred that the unknown source may be
500 relevant to solar radiation. Correlation analysis of P_{unknown} with several parameters
501 related to the processes identified as HONO sources has been widely used to diagnose
502 the unknown source. The correlations of P_{unknown} against J_{NO_2} and RH ($R^2 < 0.1$, Fig. S7
503 and S8) did not show any clear relationships. To characterize the effect of aerosol and
504 photo-enhanced NO_2 conversion on unknown HONO sources, the relationships
505 between P_{unknown} and (a) $\text{PM}_{2.5}$ concentrations, (b) $\text{PM}_{2.5} \times \text{NO}_2$, (c) $J_{\text{NO}_2} \times \text{NO}_2$, and (d)
506 $\text{PM}_{2.5} \times J_{\text{NO}_2} \times \text{NO}_2$ were analyzed, respectively. As shown in Fig. 6, the P_{unknown} increased
507 gradually with the increase of $\text{PM}_{2.5}$ concentrations, $\text{PM}_{2.5} \times \text{NO}_2$ values, $J_{\text{NO}_2} \times \text{NO}_2$
508 values and $\text{PM}_{2.5} \times J_{\text{NO}_2} \times \text{NO}_2$ values. Moreover, the positive correlations between
509 P_{unknown} and the above parameters signified that the photo-enhanced NO_2 conversion on
510 aerosol surface could act as a missing source for daytime HONO. The correlation
511 relationships obtained in this study were not as high as those in previous studies (Cui et
512 al., 2018; Jia et al., 2020; Li et al., 2018b; Wang et al., 2017). Though the researches of
513 Ziemba et al (2010), Rutter et al (2014), Leong et al (2016) and Gall et al (2016), it can
514 be learned that the heterogeneous conversion of HNO_3 on primary organic aerosol
515 emitted by motor vehicles and the homogeneous VOCs-mediated conversion of HNO_3

516 to HONO could also be the main HONO sources. Additionally, the photolysis of total
 517 nitrate (HNO_3 and particle nitrate) have been considered as potential formation
 518 pathways of ambient HONO in several other studies (Ye et al., 2016; Zhang et al., 2020;
 519 Zhou et al., 2011). However, it was a pity that HNO_3 and particulate nitrate were not
 520 observed during the sampling period. The effect of total nitrate on HONO formation
 521 could not be evaluated in this study. Considering the significant role of total nitrate, the
 522 conversion of total nitrate to HONO in ozone pollution period will be studied in the
 523 future.

524



525

526 **Fig. 6** The correlations between P_{unknown} and $\text{PM}_{2.5}$ (a), $\text{PM}_{2.5} \times \text{NO}_2$ (b), $J_{\text{NO}_2} \times \text{NO}_2$ (c)
 527 and $\text{PM}_{2.5} \times J_{\text{NO}_2} \times \text{NO}_2$ (d). Mean (blue circle), median (middle horizontal line), 25th
 528 and 75th percentiles (P25-P75, box), 10th and 90th percentiles (P10-P90, whiskers).

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530 3.5 Impact of HONO on AOC, OH and O_3 budget

531 It is known that photolysis of HONO plays a crucial role for OH radical production

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1 532 in the atmosphere. The elevated levels of daytime HONO indicated that a strong
2 533 atmospheric oxidizing capacity exists in the atmosphere in Beijing. Additionally, OH
3 534 radical acts as an important role in ozone photochemistry. Since the ozone pollution
4 535 was severe during the observation period, the production and loss rates of O₃ were also
5 536 quantified. Fig. 7 showed the simulated average diurnal profiles of AOC, primary
6 537 production rates of OH radical, O₃ production, and loss budget with and without HONO
7 538 data constraints. The meaning of “without HONO data constraints” is that the measured
8 539 HONO concentrations are not entered into the OBM model. The calculated AOC with
9 540 and without HONO constrained were up to 8.58×10^7 and 6.63×10^7 molecules cm⁻³ s⁻¹
10 541 ¹ at noon, with average daytime (7:00-19:00 LT) values of 4.33×10^7 and 3.27×10^7
11 542 molecules cm⁻³ s⁻¹, respectively. The AOC levels were relatively lower than those
12 543 determined at the same site in 2008 (Yang et al. 2018), but comparable to the values at
13 544 a background site in Hong Kong (Li et al., 2018b). This implied the decreased oxidation
14 545 capacity due to the implementation of strict emission reduction measures taken in
15 546 Beijing in recent years. OH was the predominant oxidant, as expected, accounting for
16 547 88% and 85% of the AOC with and without HONO constrained, respectively. During
17 548 the nighttime, the contributions from O₃ and NO₃ to AOC began to increase due to low
18 549 OH levels.

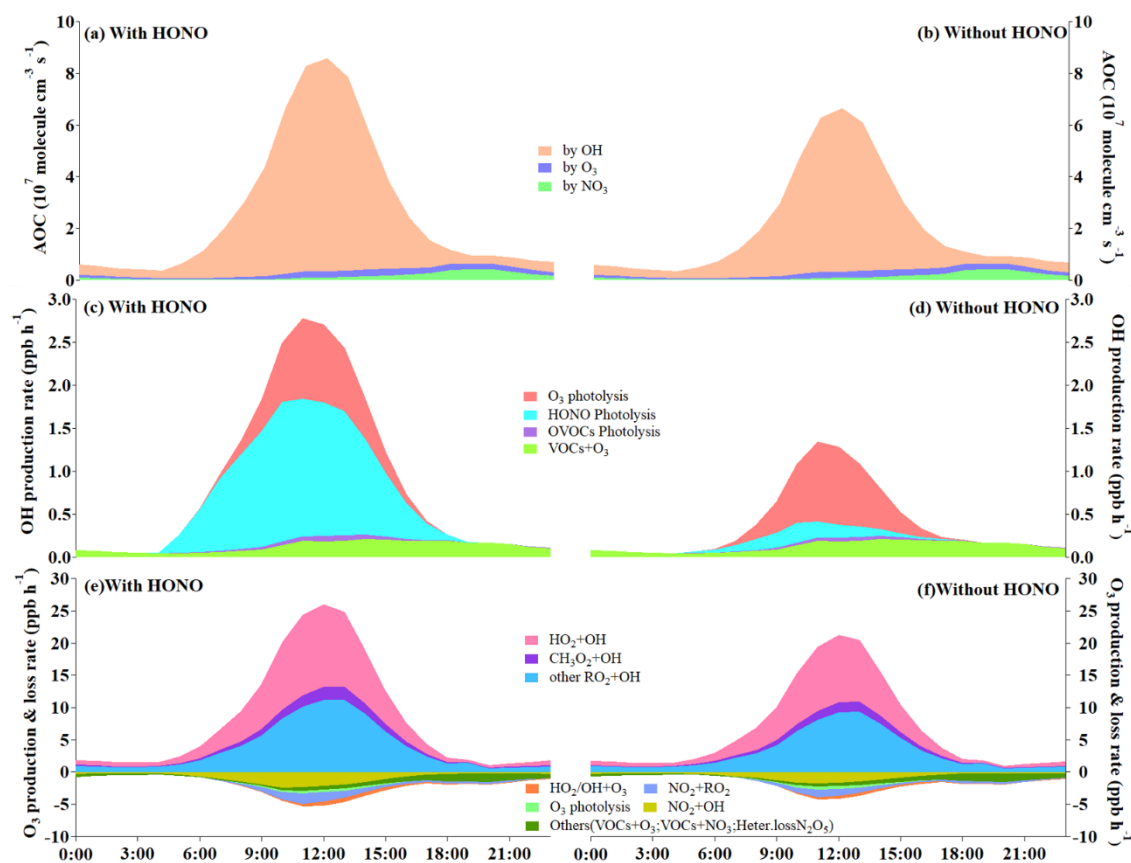
19 550 Here we calculated the production rate of OH radicals from HONO photolysis and
20 551 compared it with those from other sources, including O₃ photolysis, OVOCs photolysis
21 552 as well as ozonolysis of alkenes (Fig. 7 (c) and (d)). In terms of the daytime average,
22 553 HONO photolysis was the largest contributor to OH production with an average value
23 554 of 0.93 ppb h⁻¹, followed by O₃ photolysis (0.36 ppb h⁻¹), and ozonolysis of alkenes
24 555 (0.16 ppb h⁻¹). The contribution of OVOCs photolysis could be neglected with an
25 556 average of 0.03 ppb h⁻¹. Even at noontime, HONO photolysis still presented the
26 557 dominant contributor of OH production, which was consistent with the conclusion in
27 558 the previous study (Li et al., 2018a). When HONO concentration was not constrained,
28 559 the contribution from HONO photolysis was much underestimated reaching up to 89%
29 560 (0.10 ppb h⁻¹).

30 561 To accurately evaluate the impacts of HONO on in-situ photochemical O₃

1 562 production, the diurnal variations of O₃ production and loss rates with and without
2 563 HONO were depicted in Fig. 7 (e) and (f). The average O₃ production is dominated by
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4 564 the HO₂+NO and other RO₂+NO reactions. For the average O₃ loss, the predominate
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6 565 two pathways are NO₂+OH and NO₂+RO₂ reactions. Other reactions including
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8 566 VOCs+O₃, VOCs+NO₃, NO₂+RO₂, and Heter.lossN₂O₅ dominated the O₃ loss during
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10 567 the nighttime. All pathways except O₃ photolysis and other reactions were
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12 568 underestimated when HONO data were not constrained in the model. The net O₃
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14 569 production rate can be obtained as the difference between the production and
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16 570 destruction rate. In this study, the daytime average net production rate was 10.19 ppb h⁻¹
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18 571 with HONO constrained, which was 1.2 times higher than the value (8.18 ppb h⁻¹)
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20 572 without HONO constrained.

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23 573 Note that the homogeneous reaction of OH+NO was the only source of HONO in
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25 574 the model now, the differences of the simulated results between the two cases could
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27 575 suggest the contribution of other additional sources of HONO. The model without
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29 576 observed HONO data constraint would largely underestimate the AOC, OH production
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31 577 rate and net ozone production rate. These results verified the significant roles of HONO
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33 578 and additional HONO sources in atmospheric photochemistry. However, the direct
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35 579 HONO observations are limited in photochemical monitoring networks in China and
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37 580 the unknown sources of HONO are still unclear. To accurately simulate atmospheric
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39 581 oxidation processes, further investigation is required to figure out the mechanisms of
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41 582 HONO sources in the future.

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585 **Fig. 7** Simulated average diurnal variations of AOC (a, b), major primary OH sources
 586 (c, d) and O₃ budget (e, f) with (left panel) and without (right panel) HONO data
 587 constraints during Period II.

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589 4. Conclusions

590 High time-resolution field observation of HONO, together with other air pollutants
 591 and meteorological parameters were conducted at an urban site in Beijing from June to
 592 July 2019. A haze pollution period (Period I) and an ozone pollution period (Period II)
 593 were selected for a comparative study of two typical cases. Higher HONO
 594 concentrations and HONO/NO₂ ratios were found during Period I than those during
 595 Period II, implying that the heterogeneous conversion from NO₂ on aerosol surfaces
 596 may contribute to HONO formation. Direct vehicle emission exhibited significant
 597 contribution from 15% to 40% on ambient HONO at night. The calculated
 598 homogeneous formation rate and heterogeneous conversion frequency of NO₂ to
 599 HONO formation during Period I were higher than those during Period II. Compared

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1 600 with the homogeneous reaction of NO with OH, the heterogeneous conversion from
2 601 NO₂ was the dominant source for nocturnal HONO formation. The calculation results
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4 602 found that the daytime unknown source P_{unknown} (0.80 ppb h⁻¹) during Period II was
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6 603 higher than that (0.73 ppb h⁻¹) during Period I. Correlations analysis presented that the
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8 604 photo-enhanced NO₂ conversion on the aerosol surface appeared to be a missing HONO
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10 605 source. The model simulations showed that the oxidant reactions initiated by OH
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12 606 radicals accounted for 88% of the atmospheric oxidation capacity (AOC) during an
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14 607 ozone pollution period. HONO photolysis was the dominant source of daytime OH
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16 608 production, and the average O₃ production was dominated by the HO₂+NO and other
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18 609 RO₂+NO reactions. It could be inferred that the model without the constraint of HONO
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20 610 data would largely underestimate the AOC, OH production rates, and O₃ production
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22 611 rates in the urban atmosphere. This study provides some insight into the variation,
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24 612 sources and effect of HONO on atmospheric photochemistry in the summertime of
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26 613 Beijing. However, we will further investigate the possible sources of HONO during the
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28 614 ozone episodes and clarify the role of HONO in ozone formation by using a
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30 615 combination of field observation, experimental simulation and model simulation
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32 616 methods.
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38 **Author contributions**

39
40 619 **Yunfeng Li:** Conceptualization, Investigation, Data Curation, Writing-Original
41
42 620 Draft, Writing-Review & Editing, Visualization; **Xuezhong Wang:** Funding
43
44 621 acquisition, Resources, Supervision; **Zhenhai Wu:** Resources, Data Curation; **Ling Li:**
45
46 622 Data Curation; **Chuhan Wang:** Data Curation; **Hong Li:** Conceptualization,
47
48 623 Methodology, Writing-Review & Editing, Funding acquisition; **Xin Zhang:** Software;
49
50 624 **Yingnan Zhang:** Software, Visualization; **Junling Li:** Resources; **Rui Gao:**
51
52 625 Conceptualization, Methodology; Funding acquisition; **Likun Xue:** Methodology,
53
54 626 Software, Writing-Review & Editing; **Abdelwahid Mellouki:** Methodology,
55
56 627 Resources; **Yangang Ren:** Software, Writing-Review & Editing; **Qingzhu Zhang:**
57
58 628 Methodology.
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1 629 **Declaration of competing interest**

2
3 630 The authors declare that they have no known competing financial interests or
4
5 631 personal relationships that could have appeared to influence the work reported in this
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7 632 paper.

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33 644 **Appendix A. Supplementary data**

34
35 645 Supplementary data to this article can be found online at xxxxxxx.

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