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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
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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
5
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
39
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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23 93 As far as we know, the sources for atmospheric HONO are still not fully
24
25 94 understood. The gas-phase reaction of NO and OH is once thought to be the only
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27 95 predominant source of HONO during the daytime. However, such a mechanism could
28
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.

138 **2.2 Measurements**

139 **2.2.1 HONO measurement**

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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

1 201 also included in the model. A more detailed description of this model configuration has
2 202 been provided elsewhere (Xue et al., 2016; Xue et al., 2014; Xue et al., 2013). The
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4 203 model was constrained by the measured concentrations of O₃, SO₂, CO, NO, NO₂,
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6 204 HONO, VOCs, carbonyls, J_{NO_2} , T, P and RH at a time resolution of 5 min. For VOCs
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8 205 and carbonyl compounds, which were not measured in real-time, the time-dependent
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10 206 data were linearly interpolated into 5 min. Such approximation may lead to some
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12 207 uncertainties but should not significantly affect the estimation of the contribution of
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14 208 HONO to OH production (Jiang et al., 2020; Yang et al., 2018b).

16 209 Here our emphasis is placed on the computation of AOC, OH production rates,
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18 210 and O₃ budget. AOC is defined here as the sum of oxidation rates of VOCs and CO by
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20 211 the dominant atmospheric oxidants including OH, O₃, and NO₃ (Xue et al., 2016). The
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22 212 major primary sources of OH production include photolysis of O₃, HONO, and OVOCs
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24 213 as well as reactions of O₃+VOCs (Jiang et al., 2020; Xue et al., 2016). The ozone
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26 214 formation rates refer to the formation rates of the total oxidant (O_x=O₃+NO₂) instead
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28 215 of O₃ alone (Xue et al., 2014; Xue et al., 2013). The situ O₃ photochemical formation
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30 216 mechanism can be clarified into three pathways, HO₂+NO, CH₃O₂+NO, and other
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32 217 RO₂+NO reactions. The O₃ loss pathways include NO₂+OH, RO₂+NO₂, O₃+OH/HO₂,
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34 218 O₃ photolysis, and other reactions (VOCs+O₃, VOCs+NO₃, Heter.lossN₂O₅).
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36 219 Considering the availability of carbonyls data, the model was only performed from 22
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38 220 to 26 June (an ozone pollution period) with 00:00 local time (LT) as the initial time.
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40 221 Two model cases with and without HONO constraints were run to assess the role of
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42 222 HONO to AOC, OH production rate, and ozone budget. A six-day pre-run was made to
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44 223 stabilize the unconstrained compounds and the final outputs were extracted to further
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46 224 analyses.

225 **2.3.2 Photolysis rates and OH concentration**

51 226 The photolysis rates of HONO and O(¹D) were not measured directly in this work.
52
53 227 The J_{HONO} and $J_{\text{O}^1\text{D}}$ values can be calculated by the Tropospheric Ultraviolet and Visible
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55 228 (TUV) radiation model developed by the Nation Center for Atmospheric Research
56
57 229 (NCAR) (<http://www.acd.ucar.edu/TUV>). To reflect the influence of aerosols on J_{HONO}
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59 230 and $J_{\text{O}^1\text{D}}$ values, aerosol vertical optical depth (AOD), single scattering albedo (SSA),
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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
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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:

$$17 \quad [OH] = a \times (J_{O1D}/10^{-5} s^{-1})^b + c \quad (1)$$
$$19 \quad (a = 4.2 \times 10^6 \text{ cm}^{-3}, b = 1.0, c = 0.6 \times 10^6 \text{ cm}^{-3})$$

20
21 241 Where [OH] represents the OH concentration, J_{O1D} 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**

42 251 **3.1 Overview of measurements**

43
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 $28 \pm 4^\circ\text{C}$; the RH ranged
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50 255 from 16% to 92%, with average values of $52 \pm 18\%$. 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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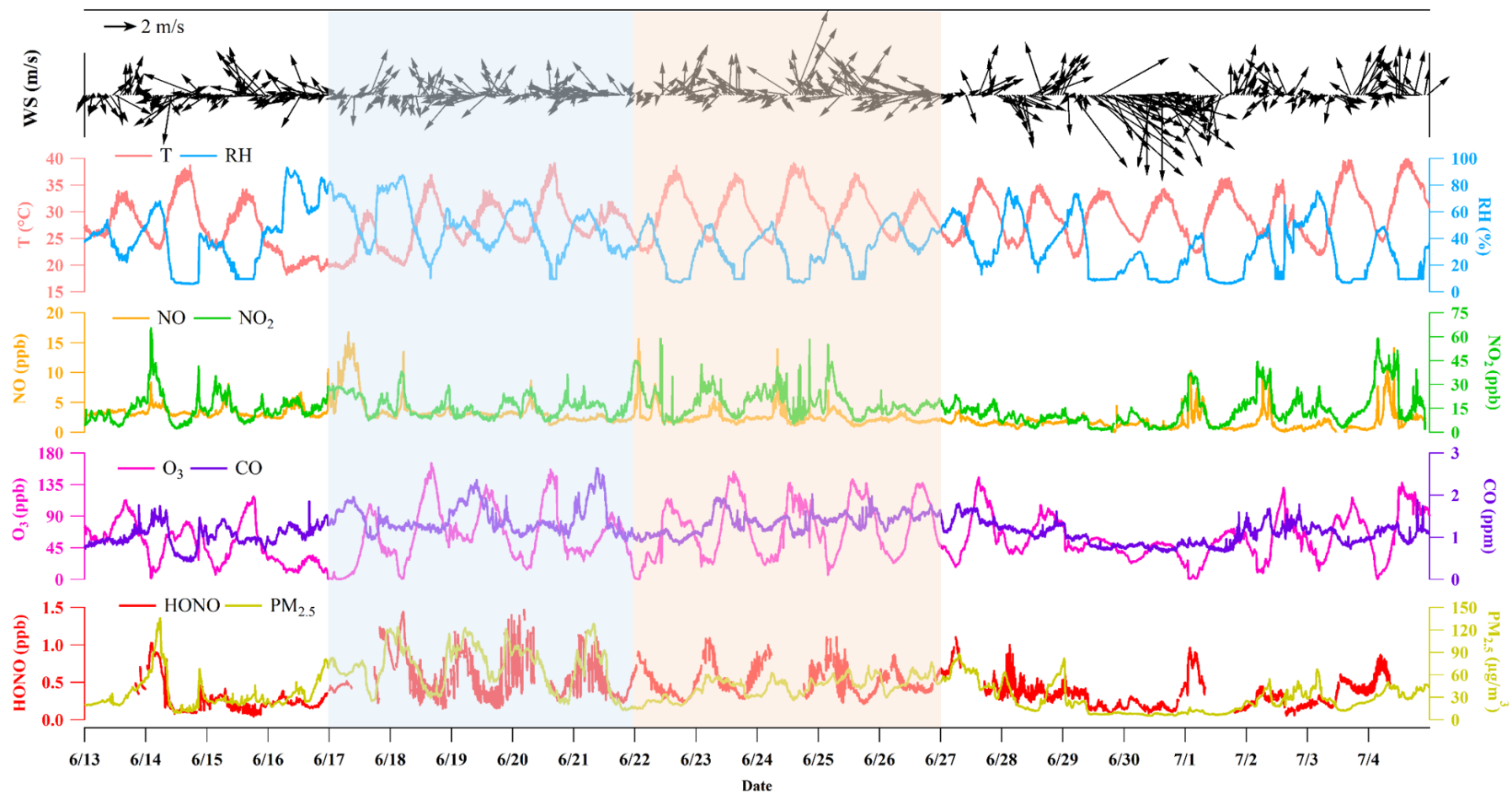


Fig. 1 Time series of HONO, O₃, CO, NO, NO₂, PM_{2.5}, and meteorological parameters from 13 June to 4 July 2019. Blue and orange areas are Period I (haze pollution) and II (ozone pollution), respectively. (Missing data are due to instrument maintenance)

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.

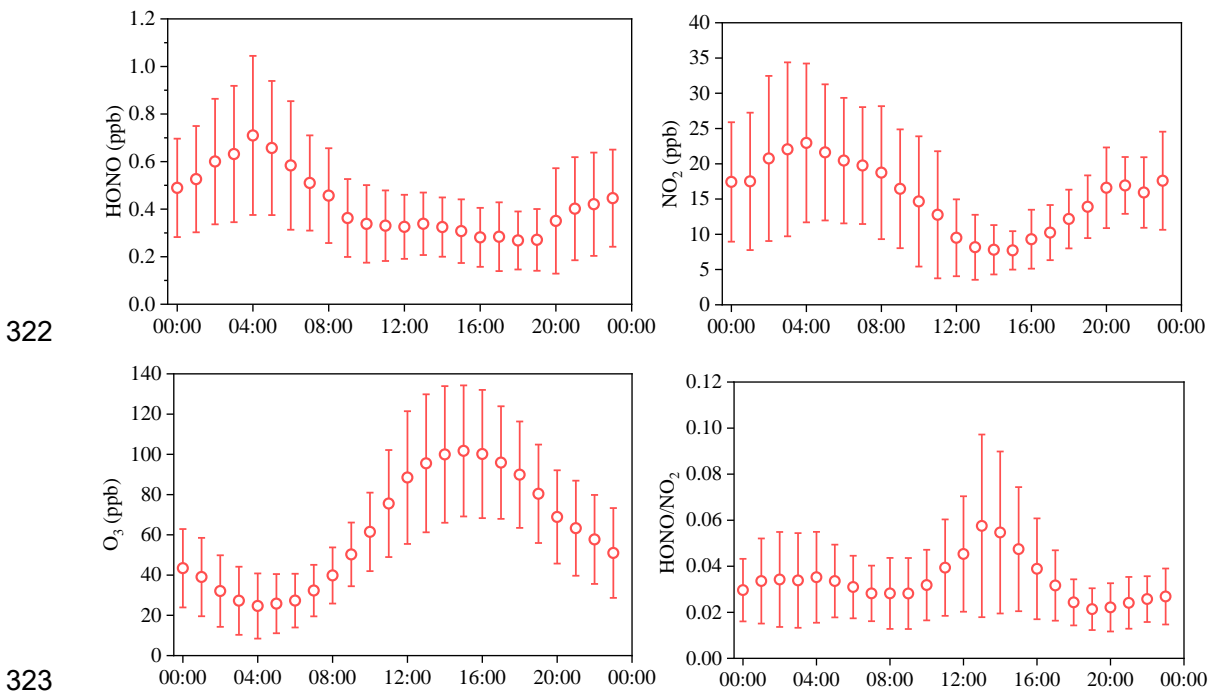


Fig. 2 Diurnal profiles of HONO, NO₂, O₃, and HONO/NO₂ ratio

(error bar means standard deviation)

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):

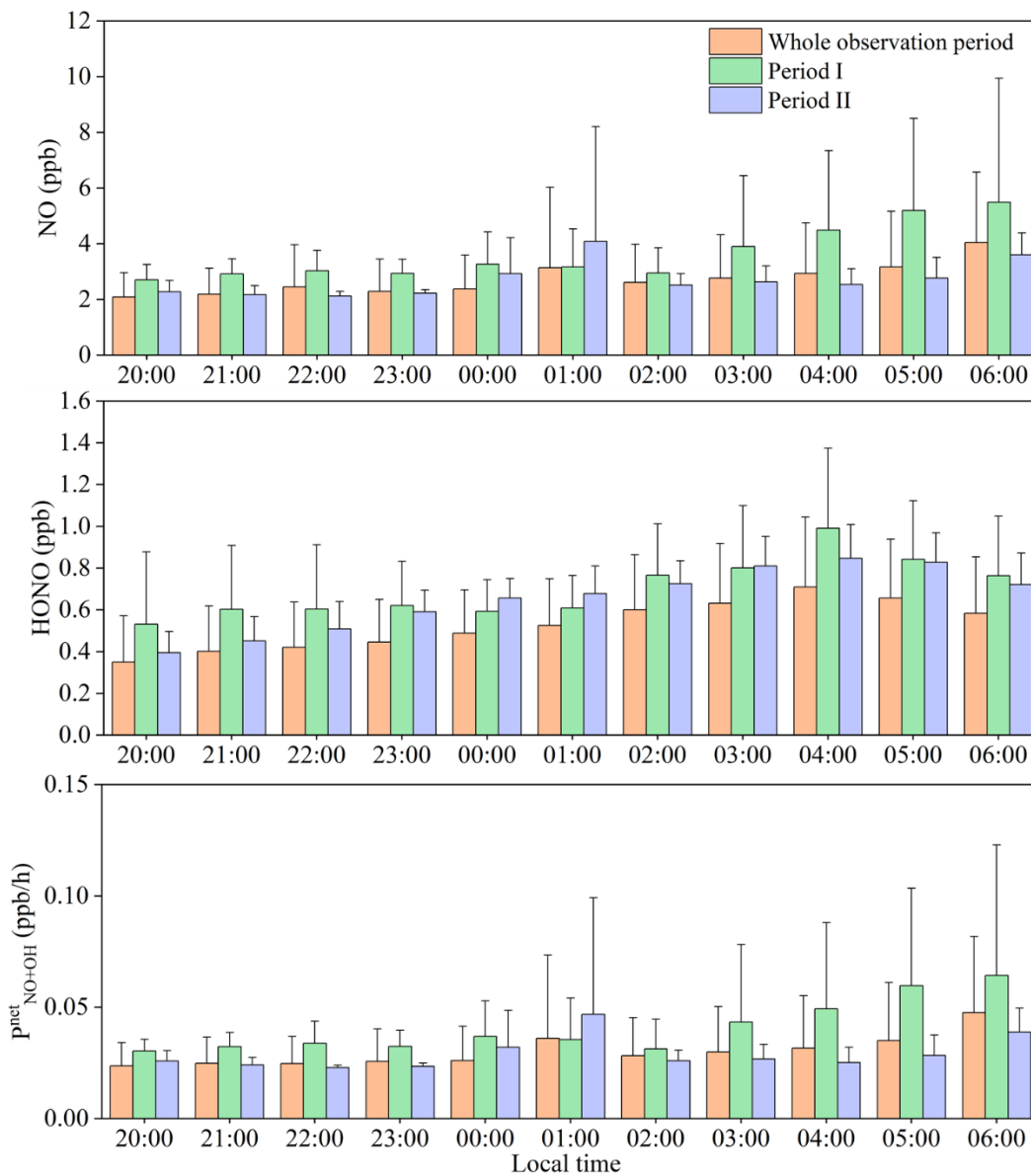


$$363 \quad P^{\text{net}}_{\text{NO+OH}} = k_{\text{NO+OH}}[\text{OH}][\text{NO}] - k_{\text{HONO+OH}}[\text{HONO}][\text{OH}] \quad (3)$$

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
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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.

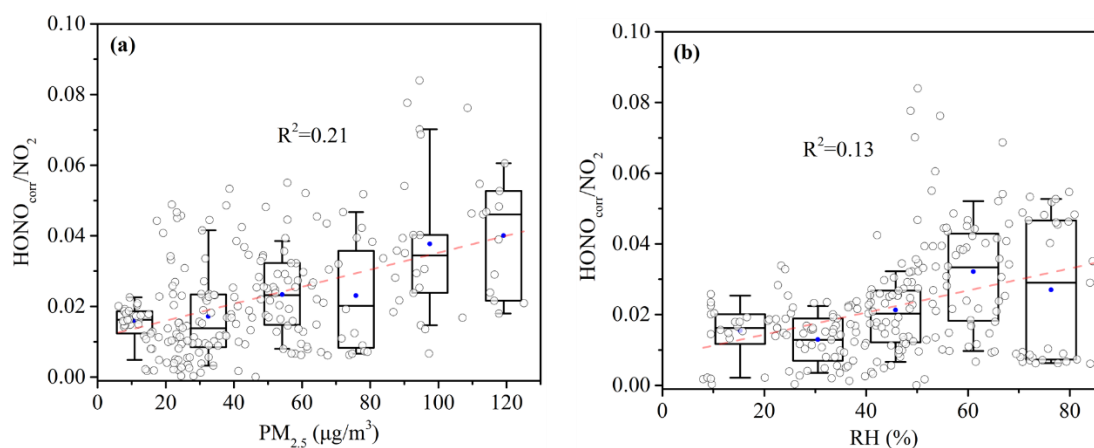


Fig. 4 The correlations between HONO_{corr}/NO₂ and PM_{2.5} concentration (a) and RH
 (b) at night. Mean (blue circle), median (middle horizontal line), 25th and 75th
 percentiles (P25-P75, box), 10th and 90th percentiles (P10-P90, whiskers).

1 460

2 3 461 **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).

$$15 \quad \frac{d[\text{HONO}]}{dt} = P_{emis} + P_{OH+NO} + P_{unknown} - L_{HONO+OH} - L_{pho} - L_{dep} \quad (7)$$

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

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

22 470 where, $d[\text{HONO}]/dt$ 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
37
38 478 daytime mixing height H in Beijing were assumed as 1.6 cm s^{-1} and 500 m, respectively.

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

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.

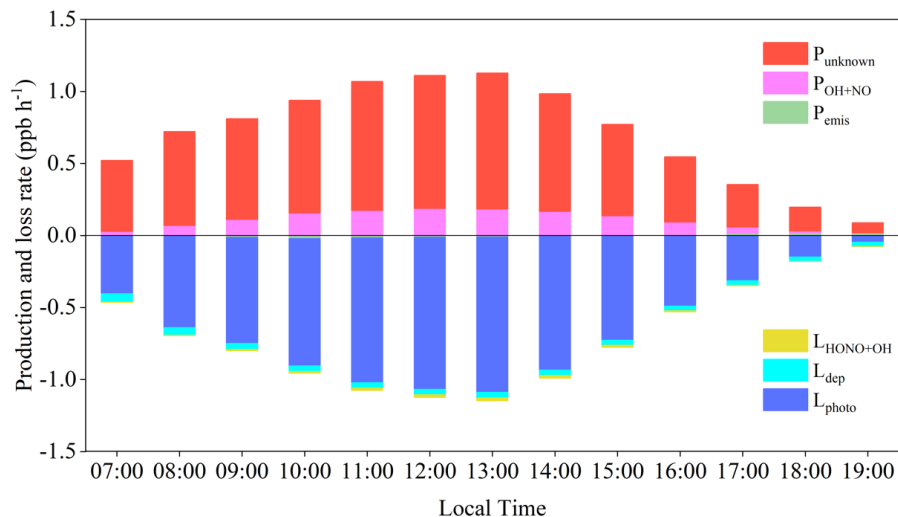
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Table 2 Comparison of the HONO concentrations and the derived P_{unknown} at different sites

| 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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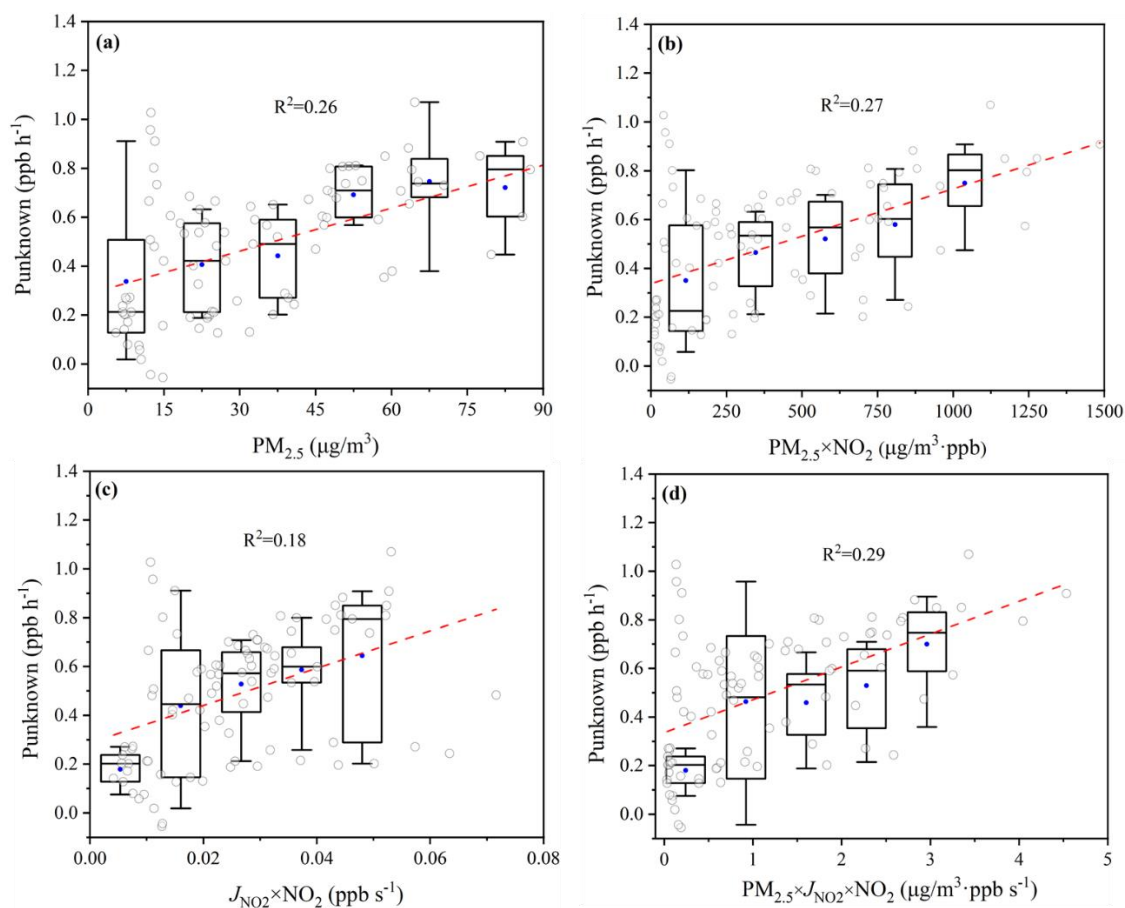


494
495 **Fig. 5** Diurnal production and loss rates for the daytime HONO budget

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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.

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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.

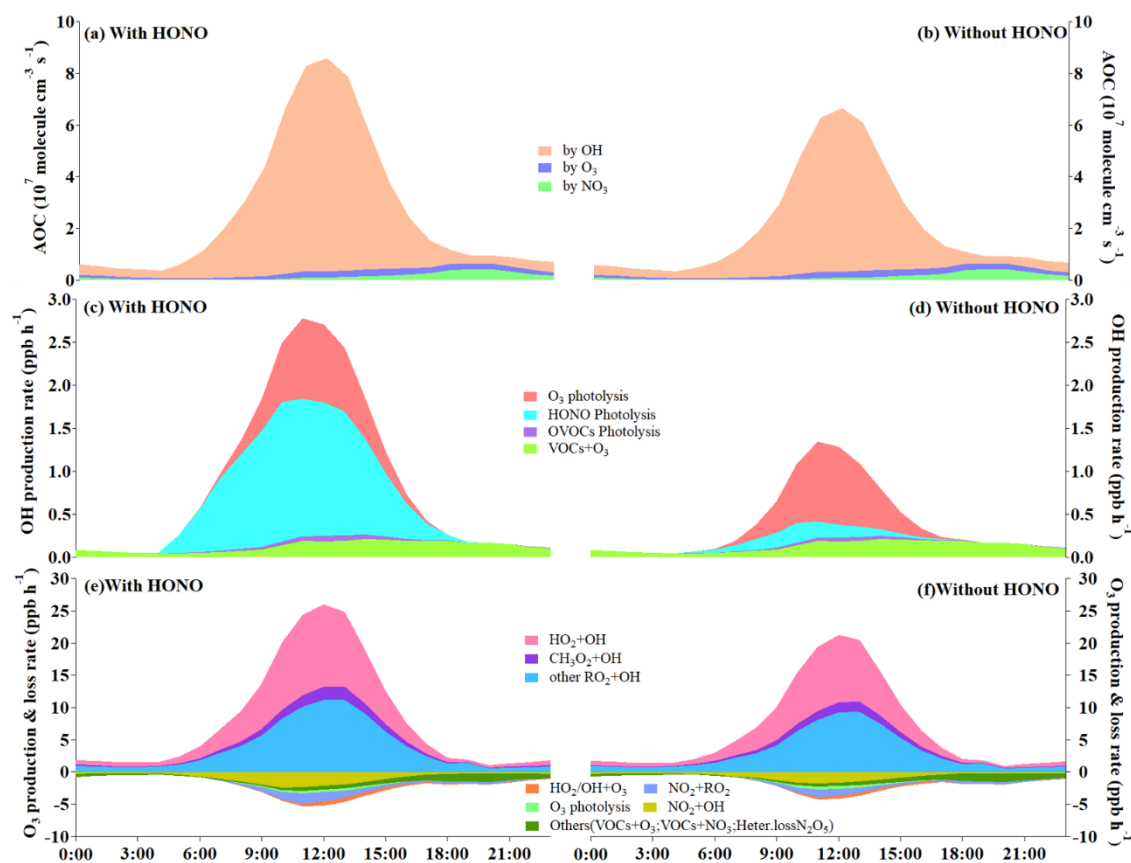
19 550 Here we calculated the production rate of OH radicals from HONO photolysis and
20 551 compared it with those from other sources, including O₃ photolysis, OVOCs photolysis
21 552 as well as ozonolysis of alkenes (Fig. 7 (c) and (d)). In terms of the daytime average,
22 553 HONO photolysis was the 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:**
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46 622 Data Curation; **Chuhan Wang:** Data Curation; **Hong Li:** Conceptualization,
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48 623 Methodology, Writing-Review & Editing, Funding acquisition; **Xin Zhang:** Software;
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50 624 **Yingnan Zhang:** Software, Visualization; **Junling Li:** Resources; **Rui Gao:**
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54 626 Software, Writing-Review & Editing; **Abdelwahid Mellouki:** Methodology,
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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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33 644 **Appendix A. Supplementary data**

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

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40 647 **References**

41
42 648 Acker, K., et al., 2006a. Nitrous acid in the urban area of Rome. *Atmos. Environ.* 40,
43
44 649 3123-3133.

45
46 650 Acker, K., et al., 2005. Concentrations of nitrous acid, nitric acid, nitrite and nitrate in
47
48 651 the gas and aerosol phase at a site in the emission zone during ESCOMPTE 2001
49
50 652 experiment. *Atmos. Res.* 74, 507-524.

51
52 653 Acker, K., et al., 2006b. Strong daytime production of OH from HNO₂ at a rural
53
54 654 mountain site. *Geophys. Res. Lett.* 33, L02809.

55
56 655 Bernard, F., et al., 2016. Measurements of nitrous acid (HONO) in urban area of
57
58 656 Shanghai, China. *Environ. Sci. Pollut. Res. Int.* 23, 5818-5829.

59
60
61
62
63
64
65

1 657 Burling, I.R., et al., 2010. Laboratory measurements of trace gas emissions from
2 658 biomass burning of fuel types from the southeastern and southwestern United
3
4 659 States. *Atmos. Chem. Phys.* 10, 11115-11130.
5
6 660 Cheng, X., et al., 2018. Atmospheric isoprene and monoterpenes in a typical urban area
7
8 661 of Beijing: Pollution characterization, chemical reactivity and source identification.
9
10 662 *J. Environ. Sci.* 71, 150-167.
11
12 663 Cui, L.L., et al., 2018. An observational study of nitrous acid (HONO) in Shanghai,
13
14 664 China: The aerosol impact on HONO formation during the haze episodes. *Sci.*
15
16 665 *Total Environ.* 630, 1057-1070.
17
18 666 Czader, B.H., et al., 2012. Modeling nitrous acid and its impact on ozone and hydroxyl
19
20 667 radical during the Texas Air Quality Study 2006. *Atmos. Chem. Phys.* 12, 6939-
21
22 668 6951.
23
24 669 Elshorbany, Y.F., et al., 2009. Oxidation capacity of the city air of Santiago, Chile.
25
26 670 *Atmos. Chem. Phys.* 9, 2257-2273.
27
28 671 Finlayson-Pitts, B.J., et al., 2003. The heterogeneous hydrolysis of NO₂ in laboratory
29
30 672 systems and in outdoor and indoor atmospheres: An integrated mechanism. *Phys.*
31
32 673 *Chem. Chem. Phys.* 5, 223-242.
33
34 674 Fu, X., et al., 2019. The significant contribution of HONO to secondary pollutants
35
36 675 during a severe winter pollution event in southern China. *Atmos. Chem. Phys.* 19,
37
38 676 1-14.
39
40 677 Gall, E.T., et al., 2016. Evaluation of nitrous acid sources and sinks in urban outflow.
41
42 678 *Atmos. Environ.* 127, 272-282.
43
44 679 Han, C., et al., 2016. Heterogeneous photochemical conversion of NO₂ to HONO on
45
46 680 the humic acid surface under simulated sunlight. *Environ. Sci. Technol.* 50, 5017-
47
48 681 5023.
49
50 682 He, Y., et al., 2006. Importance of dew in controlling the air-surface exchange of HONO
51
52 683 in rural forested environments. *Geophys. Res. Lett.* 33, L02813.
53
54 684 Heland, J., et al., 2001. A new instrument to measure gaseous nitrous acid (HONO) in
55
56 685 the atmosphere. *Environ. Sci. Technol.* 35, 3207-3212.
57
58
59 686 Hendrick, F., et al., 2014. Four years of ground-based MAX-DOAS observations of
60
61
62
63
64
65

1 687 HONO and NO₂ in the Beijing area. *Atmos. Chem. Phys.* 14, 765-781.
2
3 688 Hofzumahaus, A., et al., 2009. Amplified trace gas removal in the troposphere. *Science*
4
5 689 324, 1702-1704.
6
7 690 Hou, S., et al., 2016. Comparison of atmospheric nitrous acid during severe haze and
8
9 691 clean periods in Beijing, China. *Atmos. Environ.* 124, 199-206.
10
11 692 Huang, R.J., et al., 2017. Concentration and sources of atmospheric nitrous acid
12
13 693 (HONO) at an urban site in Western China. *Sci. Total Environ.* 593-594, 165-172.
14
15 694 Jenkin, M.E., et al., 2003. Protocol for the development of the Master Chemical
16
17 695 Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile
18
19 696 organic compounds. *Atmos. Chem. Phys.* 3, 181-193.
20
21 697 Jia, C.H., et al., 2020. Pollution characteristics and potential sources of nitrous acid
22
23 698 (HONO) in early autumn 2018 of Beijing. *Sci. Total Environ.* 735, 139317.
24
25 699 Jiang, Y., et al., 2020. Sources of nitrous acid (HONO) in the upper boundary layer and
26
27 700 lower free troposphere of the North China Plain: insights from the Mount Tai
28
29 701 Observatory. *Atmos. Chem. Phys.* 20, 12115-12131.
30
31 702 Kang, C. M., et al., 2006. Source identification and trends in concentrations of gaseous
32
33 703 and fine particulate principal species in Seoul, South Korea. *J. Air Waste Manage.*
34
35 704 56, 911-921.
36
37 705 Kleffmann, J., et al., 2005. Daytime formation of nitrous acid: A major source of OH
38
39 706 radicals in a forest. *Geophys. Res. Lett.* 32, 347-354.
40
41 707 Kleffmann, J., et al., 2003. Measured and simulated vertical profiles of nitrous acid-
42
43 708 Part I: Field measurements. *Atmos. Environ.* 37, 2949-2955.
44
45 709 Kurtenbach, R., et al., 2001. Investigations of emissions and heterogeneous formation
46
47 710 of HONO in a road traffic tunnel. *Atmos. Environ.* 35, 3385-3394.
48
49 711 Leong, Y.J., et al., 2016. Impact of environmental variables on the reduction of nitric
50
51 712 acid by proxies for volatile organic compounds emitted by motor vehicles. *Atmos.*
52
53 713 *Pollut. Res.* 7, 221-227.
54
55 714 Li, D.D., et al., 2018a. Characteristics and sources of nitrous acid in an urban
56
57 715 atmosphere of northern China: Results from 1-yr continuous observations. *Atmos.*
58
59 716 *Environ.* 182, 296-306.
60
61
62
63
64
65

1 717 Li, X., et al., 2012. Exploring the atmospheric chemistry of nitrous acid (HONO) at a
2 rural site in Southern China. *Atmos. Chem. Phys.* 12, 1497-1513.
3
4 719 Li, Y., et al., 2011. Impacts of HONO sources on the air quality in Beijing, Tianjin and
5 Hebei Province of China. *Atmos. Environ.* 45, 4735-4744.
6
7 720
8 721 Li, Z.Y., et al., 2018b. Oxidizing capacity of the rural atmosphere in Hong Kong,
9 Southern China. *Sci. Total Environ.* 612, 1114-1122.
10
11 722
12 723 Liu, Y., et al., 2017. Direct emission of nitrous acid (HONO) from gasoline cars in
13 China determined by vehicle chassis dynamometer experiments. *Atmos. Environ.*
14
15 724 169, 89-96.
16
17 725
18 726 Liu, Y., et al., 2019. Semi-quantitative understanding of source contribution to nitrous
19 acid (HONO) based on 1 year of continuous observation at the SORPES station in
20 eastern China. *Atmos. Chem. Phys.* 19, 13289-13308.
21
22 727
23 728
24 729 Liu, Y., et al., 2020. The promotion effect of nitrous acid on aerosol formation in
25 wintertime in Beijing: the possible contribution of traffic-related emissions. *Atmos.*
26
27 730
28
29 731
30
31 732 Liu, Z., et al., 2014. Evidence of aerosols as a media for rapid daytime HONO
32 production over China. *Environ. Sci. Technol.* 48, 14386-14391.
33
34 733
35 734 Lu, K.D., et al., 2014. Nighttime observation and chemistry of HOx in the Pearl River
36 Delta and Beijing in summer 2006. *Atmos. Chem. Phys.* 14, 4979-4999.
37
38 735
39 736 Ma, Q.X., et al., 2017. SO₂ initiates the efficient conversion of NO₂ to HONO on MgO
40 surface. *Environ. Sci. Technol.* 51, 3767-3775.
41
42 737
43 738 Meng, F., et al., 2020. High-resolution vertical distribution and sources of HONO and
44 NO₂ in the nocturnal boundary layer in urban Beijing, China. *Atmos. Chem. Phys.*
45
46 739 20, 5071-5092.
47
48 740
49
50 741 Michoud, V., et al., 2014. Study of the unknown HONO daytime source at a European
51 suburban site during the MEGAPOLI summer and winter field campaigns. *Atmos.*
52
53 742
54 743
55
56 744 Monge, M.E., et al., 2010. Light changes the atmospheric reactivity of soot. *Proc. Natl.*
57
58 745
59
60 746 Nakashima, Y., Kajii, Y., 2017. Determination of nitrous acid emission factors from a
61
62
63
64
65

1 747 gasoline vehicle using a chassis dynamometer combined with incoherent
2 748 broadband cavity-enhanced absorption spectroscopy. *Sci. Total Environ.* 575, 287-
3
4 749 293.
5
6 750 Nakashima, Y., et al., 2017. Contributions of vehicular emissions and secondary
7
8 751 formation to nitrous acid concentrations in ambient urban air in Tokyo in the winter.
9
10 752 *Sci. Total Environ.* 592, 178-186.
11
12 753 Nie, W., et al., 2015. Influence of biomass burning plumes on HONO chemistry in
13
14 754 eastern China. *Atmos. Chem. Phys.* 15, 1147-1159.
15
16 755 Qin, M., et al., 2009. An observational study of the HONO-NO₂ coupling at an urban
17
18 756 site in Guangzhou City, South China. *Atmos. Environ.* 43, 5731-5742.
19
20 757 Ren, X., et al., 2003. OH and HO₂ Chemistry in the urban atmosphere of New York
21
22 758 City. *Atmos. Environ.* 37, 3639-3651.
23
24 759 Ren, Y., et al., 2020. Role of the dew water on the ground surface in HONO distribution:
25
26 760 a case measurement in Melpitz. *Atmos. Chem. Phys.* 20, 13069-13089.
27
28 761 Rohrer, F., Berresheim, H., 2006. Strong correlation between levels of tropospheric
29
30 762 hydroxyl radicals and solar ultraviolet radiation. *Nature.* 442, 184-187.
31
32 763 Rutter, A.P., et al., 2014. The reduction of HNO₃ by volatile organic compounds emitted
33
34 764 by motor vehicles. *Atmos. Environ.* 87, 200-206.
35
36 765 Saunders, S.M., et al., 2003. Protocol for the development of the Master Chemical
37
38 766 Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile
39
40 767 organic compounds. *Atmos. Chem. Phys.* 3, 161-180.
41
42 768 Shi, X., et al., 2020. Budget of nitrous acid and its impacts on atmospheric oxidative
43
44 769 capacity at an urban site in the central Yangtze River Delta region of China. *Atmos.*
45
46 770 *Environ.* 238, 117725.
47
48 771 Sorgel, M., et al., 2011. Quantification of the unknown HONO daytime source and its
49
50 772 relation to NO₂. *Atmos. Chem. Phys.* 11, 10433-10447.
51
52 773 Spataro, F., Ianniello, A., 2014. Sources of atmospheric nitrous acid: state of the science,
53
54 774 current research needs, and future prospects. *J. Air Waste Manag. Assoc.* 64, 1232-
55
56 775 1250.
57
58 776 Spataro, F., et al., 2013. Occurrence of atmospheric nitrous acid in the urban area of
59
60
61
62
63
64
65

1 777 Beijing (China). *Sci. Total Environ.* 447, 210-224.
2 778 Spataro, F., et al., 2017. Sources of atmospheric nitrous acid (HONO) in the European
3 High Arctic. *Rend. Fis. Acc. Lincei.* 28, 25-33.
4 779
5
6 780 Stutz, J., et al., 2004. Relative humidity dependence of HONO chemistry in urban areas.
7
8 781 *J. Geophys. Res.* 109, D03307.
9
10 782 Stutz, J., Björn A., and Albrecht N., 2002. Nitrous acid formation in the urban
11 atmosphere: Gradient measurements of NO₂ and HONO over grass in Milan, Italy.
12 783
13
14 784 *J. Geophys. Res.*, 107, 8192.
15
16 785 Su, H., et al., 2011. Soil nitrite as a source of atmospheric HONO and OH radicals.
17
18 786 *Science.* 333, 1616-1618.
19
20 787 Su, H., et al., 2008a. Observation of nighttime nitrous acid (HONO) formation at a non-
21 urban site during PRIDE-PRD2004 in China. *Atmos. Environ.* 42, 6219-6232.
22 788
23 789 Su, H., et al., 2008b. Nitrous acid (HONO) and its daytime sources at a rural site during
24 the 2004 PRIDE-PRD experiment in China. *J. Geophys. Res.* 113, D14312.
25 790
26
27 791 Tan, Z., et al., 2018. Wintertime photochemistry in Beijing: observations of ROx radical
28 concentrations in the North China Plain during the BEST-ONE campaign. *Atmos.*
29 *Chem. Phys.* 18, 12391-12411.
30 792
31 793
32
33 794 Tong, S., et al., 2015. Comparisons of measured nitrous acid (HONO) concentrations
34 in a pollution period at urban and suburban Beijing, in autumn of 2014. *J. Sci.*
35 *China Chem.* 58, 1393-1402.
36 795
37 796
38
39 797 USEPA. 1999. Compendium method TO-11A determination of formaldehyde in
40 ambient air using adsorbent cartridge followed by high performance liquid
41 chromatography (HPLC). *Compendium of Methods for the Determination of*
42 *Toxic Organic Compounds in Ambient Air. Second Edition.*
43 798
44 799
45 800
46
47 801 Villena, G., et al., 2011. Nitrous acid (HONO) during polar spring in Barrow, Alaska:
48 A net source of OH radicals? *J. Geophys. Res.* 116, D00R07.
49 802
50 803 Wang, J., et al., 2017. Observation of nitrous acid (HONO) in Beijing, China: Seasonal
51 variation, nocturnal formation and daytime budget. *Sci. Total Environ.* 587-588,
52 350-359.
53 804
54 805
55 806 Wang, S., et al., 2013. Long-term observation of atmospheric nitrous acid (HONO) and
56
57
58
59
60
61
62
63
64
65

1 807 its implication to local NO₂ levels in Shanghai, China. *Atmos. Environ.* 77, 718-
2 808 724.
3
4 809 Winer, A.M., Biermann, H.W., 1994. Long pathlength differential optical absorption
5 spectroscopy (DOAS) measurements of gaseous HONO, NO₂ and HCNO in the
6 810 California South Coast Air Basin. *Res. Chem. Intermed.* 20, 423-445.
7 811
8 812 Xu, Z., et al., 2015. Nitrous acid (HONO) in a polluted subtropical atmosphere:
9 Seasonal variability, direct vehicle emissions and heterogeneous production at
10 813 ground surface. *Atmos. Environ.* 106, 100-109.
11 814
12 815 Xu, Z., et al., 2013. Evaluating the uncertainties of thermal catalytic conversion in
13 measuring atmospheric nitrogen dioxide at four differently polluted sites in China.
14 816 *Atmos. Environ.* 76, 221-226.
15 817
16 818 Xue, C., et al., 2020. HONO budget and its role in nitrate formation in the rural North
17 819 China Plain. *Environ. Sci. Technol.* 54, 11048-11057.
18 820
19 821 Xue, L.K., et al., 2016. Oxidative capacity and radical chemistry in the polluted
20 atmosphere of Hong Kong and Pearl River Delta region: analysis of a severe
21 822 photochemical smog episode. *Atmos. Chem. Phys.* 16, 9891-9903.
22 823
23 824 Xue, L.K., et al., 2014. Ground-level ozone in four Chinese cities: precursors, regional
24 transport and heterogeneous processes. *Atmos. Chem. Phys.* 14, 13175-13188.
25 825
26 826 Xue, L.K., et al., 2013. Sources and photochemistry of volatile organic compounds in
27 the remote atmosphere of western China: Results from the Mt. Waliguan
28 827 Observatory. *Atmos. Chem. Phys.* 13, 8551-8567.
29 828
30 829 Yang, Q., et al., 2014. Daytime HONO formation in the suburban area of the megacity
31 Beijing, China. *Sci. China Chem.* 57, 1032-1042.
32 830
33 831 Yang, W., et al., 2018a. Significant HONO formation by the photolysis of nitrates in the
34 presence of humic acids. *Environ. Pollut.* 243, 679-686.
35 832
36 833 Yang, W., et al., 2020. Heterogenous photochemical uptake of NO₂ on the soil surface
37 as an important ground-level HONO source. *Environ. Pollut.* 271, 116289.
38 834
39 835 Yang, X., et al., 2018b. Observations and explicit modeling of summertime carbonyl
40 formation in Beijing: Identification of key precursor species and their impact on
41 atmospheric oxidation chemistry. *J. Geophys. Res. Atmos.* 123, 1426-1440.
42 836
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 837 Yang, X., et al., 2017. Carbonyl compounds at Mount Tai in the North China Plain:
2 838 Characteristics, sources, and effects on ozone formation. *Atmos. Res.* 196, 53-61.
3
4 839 Ye, C.X., et al., 2016. Photolysis of nitric acid and nitrate on natural and artificial
5 840 surfaces. *Environ. Sci. Technol.* 50, 3530-3536.
6
7 841 Yu, X.N., Zhu, B., Zhang, M.G., 2009a. Seasonal variability of aerosol optical
8 842 properties over Beijing. *Atmos. Environ.* 43, 4095-4101.
9
10 843 Yu, Y., et al., 2009b. Observations of high rates of NO₂-HONO conversion in the
11 844 nocturnal atmospheric boundary layer in Kathmandu, Nepal. *Atmos. Chem. Phys.*
12 845 9, 6401-6415.
13
14 846 Yun, H., et al., 2017. Nitrous acid in a street canyon environment: Sources and
15 847 contributions to local oxidation capacity. *Atmos. Environ.* 167, 223-234.
16
17 848 Zhang, H., et al., 2017. Atmospheric volatile organic compounds in a typical urban area
18 849 of Beijing: Pollution characterization, health Risk assessment and source
19 850 apportionment. *Atmosphere.* 8, 61.
20
21 851 Zhang, J.W., et al., 2019a. Impacts of potential HONO sources on the concentrations of
22 852 oxidants and secondary organic aerosols in the Beijing-Tianjin-Hebei region of
23 853 China. *Sci. Total Environ.* 647, 836-852.
24
25 854 Zhang, W.Q., et al., 2019b. Variations and sources of nitrous acid (HONO) during a
26 855 severe pollution episode in Beijing in winter 2016. *Sci. Total Environ.* 648, 253-
27 856 262.
28
29 857 Zhang, W.Q., et al., 2020. Different HONO sources for three layers at the urban area of
30 858 Beijing. *Environ. Sci. Technol.* 54, 12870-12880.
31
32 859 Zhang, X., et al., 2019c. Optimization and preliminary application of the detection
33 860 method of carbonyl compounds in the ambient air. *Res. Environ.Sci.* 32, 821-829.
34
35 861 Zheng, H., et al., 2020. Contribution of particulate nitrate photolysis to heterogeneous
36 862 sulfate formation for winter haze in China. *Environ. Sci. Technol Lett.* 7, 632-638.
37
38 863 Zhou, X., et al., 2011. Nitric acid photolysis on forest canopy surface as a source for
39 864 tropospheric nitrous acid. *Nat. Geosci.* 4, 440-443.
40
41 865 Zhou, X.L., et al., 2007. Summertime observations of HONO, HCHO, and O₃ at the
42 866 summit of Whiteface Mountain, New York. *J. Geophys. Res. Atmos.* 112, D08311.
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65

867 Ziemba, L.D., et al., 2010. Heterogeneous conversion of nitric acid to nitrous acid on
868 the surface of primary organic aerosol in an urban atmosphere. Atmos. Environ.
869 44, 4081-4089.
870