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Dandan Li, Likun Xue, Liang Wen, Xinfeng Wang, Tianshu Chen, et al.. Characteristics and sources of nitrous acid in an urban atmosphere of northern China: Results from 1-yr continuous observations. Atmospheric Environment, 2018, 182, pp.296-306. 10.1016/j.atmosenv.2018.03.033 . insu-01744529

HAL Id: insu-01744529

<https://insu.hal.science/insu-01744529>

Submitted on 27 Mar 2018

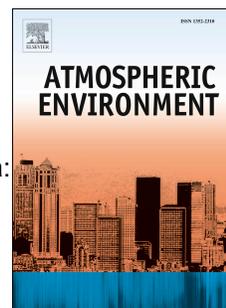
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Accepted Manuscript

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PII: S1352-2310(18)30185-7

DOI: [10.1016/j.atmosenv.2018.03.033](https://doi.org/10.1016/j.atmosenv.2018.03.033)

Reference: AEA 15903

To appear in: *Atmospheric Environment*

Received Date: 13 July 2017

Revised Date: 27 February 2018

Accepted Date: 18 March 2018

Please cite this article as: Li, D., Xue, L., Wen, L., Wang, X., Chen, T., Mellouki, A., Chen, J., Wang, W., Characteristics and sources of nitrous acid in an urban atmosphere of northern China: Results from 1-yr continuous observations, *Atmospheric Environment* (2018), doi: 10.1016/j.atmosenv.2018.03.033.

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Characteristics and sources of nitrous acid in an urban atmosphere of northern China:**Results from 1-yr continuous observations**

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Abstract

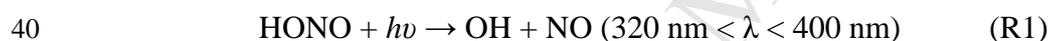
Nitrous acid (HONO) is a key reservoir of the hydroxyl radical (OH) and plays a central role in the atmospheric chemistry. To understand the sources and impact of HONO in the polluted atmosphere of northern China, continuous measurements of HONO and related parameters were conducted from September 2015 to August 2016 at an urban site in Ji'nan, the capital city of Shandong province. HONO showed well-defined seasonal and diurnal variation patterns with clear wintertime and nighttime concentration peaks. Elevated HONO concentrations (e.g., over 5 ppbv) were frequently observed with a maximum value of 8.36 ppbv. The HONO/NO_x ratios of direct vehicle emissions varied in the range of 0.29%-0.87%, with a mean value of 0.53%. An average NO₂-to-HONO nighttime conversion frequency (k_{het}) was derived to be $0.0068 \pm 0.0045 \text{ h}^{-1}$ from 107 HONO formation cases. A detailed HONO budget analysis suggests an unexplained daytime missing source of 2.95 ppb h⁻¹ in summer, which is about seven times larger than the homogeneous reaction of NO with OH. The effect of HONO on OH production was also quantified. HONO photolysis was the uppermost source of local OH radical throughout the daytime. This study provides the year-round

27 continuous record of ambient HONO in the North China Plain, and offers some insights into
28 the characteristics, sources and impacts of HONO in the polluted atmospheres of China.

29 **Keywords:** Nitrous acid, Seasonal variation, Heterogeneous conversion, Atmospheric
30 oxidizing capacity, North China Plain

31 **1. Introduction**

32 Nitrous acid (HONO) is a key precursor of the hydroxyl radical (OH), one of the main
33 tropospheric oxidants in the gas phase. Numerous field and modeling studies have shown that
34 HONO photolysis contributes significantly to the OH sources not only in the early morning
35 but also during the rest of the daytime (Acker et al., 2006b; Kleffmann et al., 2005; Xue et al.,
36 2016). This is mainly ascribed to the unexpectedly high concentrations of HONO during
37 daytime which would have been kept at lower levels due to its rapid photolysis (R1).
38 Therefore, the knowledge of characteristics and sources of HONO is critical for a better
39 understanding of the tropospheric oxidation chemistry processes.

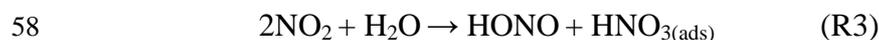


41 So far, field observations of HONO have been carried out at remote, rural and urban
42 areas. The reported ambient concentrations rang from several pptv up to 15 ppbv (e.g., Beine
43 et al., 2006; Elshorbany et al., 2009; Zhou et al., 2001). However, the potential sources that
44 could explain the observed elevated daytime HONO are still under controversial discussion.
45 The well accepted HONO sources include direct emissions from vehicle exhaust (Kurtenbach
46 et al., 2001) and homogeneous gas phase reaction of NO with OH (R2) (Pagsberg et al.,
47 1997).

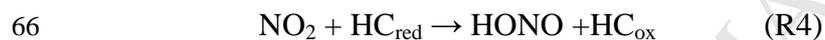


49 Heterogeneous reactions of NO₂ occurring on wet surfaces (R3) have been also proposed as
50 an important source of HONO according to both laboratory studies and field observations
51 (e.g., Finlayson-Pitts et al., 2003). Nonetheless, the source strength of reaction (R3) has not
52 been accurately quantified and relies on the NO₂ concentrations, surface area density and
53 water content (Finlayson-Pitts et al., 2003). These reactions could occur on various types of

54 surfaces including ground, buildings, vegetation, and aerosol surfaces (Liu et al., 2014;
55 VandenBoer et al., 2013). Up to now, the contribution of the ground surfaces to the overall
56 production of HONO is still under discussion and subject to intensive research activity (Wong
57 et al., 2011; Zhang et al., 2016).



59 In addition, the heterogeneous reduction of NO_2 on soot particles, mineral dust, and surfaces
60 containing organic substrates was also proposed as a source of HONO (R4) (Ammann et al.,
61 1998 and 2005; Ma et al., 2017), and these processes can be further photo-enhanced during
62 the daytime (George et al., 2005; Monge et al., 2010; Ndour et al., 2008; Stemmler et al.,
63 2006). Although the heterogeneous NO_2 conversion on soot surfaces has high potential to
64 produce HONO, it decreases rapidly with aging and is usually regarded to be less important
65 for ambient HONO formation (Han et al., 2013).



67 Besides, some other HONO sources have also been proposed, including soil emissions (Su et
68 al., 2011), photolysis of adsorbed nitric acid (HNO_3) and nitrate (NO_3^-) at UV wavelengths of
69 300 nm (Zhou et al., 2001), and homogeneous reaction of NO_2 with $\text{HO}_2 \cdot \text{H}_2\text{O}$ (Li et al.,
70 2014). Despite the abovementioned significant progress, the ‘missing’ daytime source(s) of
71 atmospheric HONO is still under exploration.

72 In comparison with sources, the sink pathways of HONO are relatively well established.
73 The chemical losses of HONO include the photolysis (R1) and reactions with OH radicals
74 (R5). Moreover, HONO can be also removed through dry deposition on ground surfaces.
75 Budget analysis of HONO sources and sinks has been proved to be a robust method to
76 examine the unknown sources and quantify their source strength (Sörgel et al., 2011; Su et al.,
77 2008b).



79 A number of field studies have been conducted to measure ambient HONO in the
80 polluted urban and rural atmospheres of China during the last decade. High concentration

81 levels and strong potential missing source(s) of HONO have been reported in some
82 metropolises (e.g., Beijing, Shanghai and Guangzhou) and surrounding regions (e.g., Bernard
83 et al., 2016; Qin et al., 2009; Tong et al., 2016). However, most of these studies were mainly
84 based on short-term intensive observations. While long-period measurements are necessary to
85 support a holistic investigation of characteristics and sources of HONO, they are very scarce
86 (Hendrick et al., 2014). In the present study, we have carried out 1-yr continuous observations
87 of HONO and related parameters at an urban site of Ji'nan city, which is located almost in the
88 center of the North China Plain (NCP), the most polluted region of China with dense
89 population and industries. A large amount of observational data and HONO formation cases
90 provided an opportunity of a thorough examination of temporal variations, sources and
91 impacts of HONO in this polluted urban atmosphere of northern China. In the following
92 sections, we will first show the seasonal and diurnal variations of HONO and related species.
93 Then, several sources of HONO will be explored, including vehicle emission, nighttime
94 heterogeneous formation and potential unknown daytime sources. We will finally evaluate
95 the impacts of HONO photolysis on the primary OH sources and hence atmospheric
96 oxidizing capacity.

97 **2. Experimental**

98 **2.1. Site description**

99 The measurements were conducted from September 1st 2015 to August 31st 2016 at an
100 urban site of Ji'nan, the capital city of Shandong Province, with approximately 7 million
101 population and 1.6 million automobiles. The site is located in the central campus of Shandong
102 University (36°40'N, 117°03'E), a typical urban area surrounded by massive buildings and
103 condensed population and close to several main traffic roads (Fig.1). Large-scale industries,
104 including steel plants, thermal power plants, cement plants, oil refineries and chemical plants
105 in suburban areas are the major industrial emission sources of local air pollution in Ji'nan,
106 and are mainly distributed in the northeast and southwest of the site. By observing the spikes
107 of sulfur dioxide (SO₂) concentrations under northeasterly and/or southwesterly winds, we
108 know that the site was affected by the local industrial emission sources. All the measurements
109 were carried out on the rooftop of a six-floor teaching building, around 22 m above the

110 ground level. A detailed description of the study site can be found elsewhere (Wang et al.,
111 2015).

112 **2.2. Measurement techniques**

113 HONO was measured by a commercial instrument of LOPAP (long path absorption
114 photometer, *QUMA GmbH, Germany*). The LOPAP is a wet chemistry based real-time
115 measurement device, with which HONO is sampled in an external sampling unit as a stable
116 diazonium salt and is subsequently detected photo-metrically after conversion into an azodye
117 in a long-path absorption tube of 2.4 m Teflon AF. The LOPAP is conceived as a 2-channel
118 system to correct for the potential interferences. In channel 1, HONO as well as possible
119 interfering gases are determined, while in channel 2 only the interfering gases are quantified.
120 The difference of both channels yields the HONO concentrations. A detailed description of
121 the LOPAP instrument has been described in detail by Heland et al. (2001). In the present
122 study, the sampling gas flow and the peristaltic pump velocity were set to 1 L min^{-1} and 20 r
123 min^{-1} during the whole measurement period. With these settings, the HONO collection
124 efficiency was ensured above 99.99%. Zero air calibration by ultrapure nitrogen (purity of
125 99.999%) was performed for 30 min automatically at a time interval of 12 h 30 min. An
126 experimental cycle of 8 days was calibrated twice manually by using a known concentration
127 of nitrite (NO_2^-) standard solution. The detection limit of our measurements was 3 ppt at a
128 time resolution of 30 s, with an accuracy of 10% and a precision of 1%. We note that
129 although the LOPAP instrument may collect data in 30 s (or 1 min) intervals, the physical
130 time resolution of the instrument is relatively longer, ca. 3 min.

131 The NO and NO_2 concentrations were measured by a chemiluminescence NO- NO_2 - NO_x
132 analyzer (*Model 42C, TEC, USA*) with a time resolution of 1 min, in which NO_2 was
133 converted to NO by a molybdenum oxide (MoO) catalytic converter. It should be noted that
134 the MoO converters may also convert some NO_z species to NO and hence overestimate the
135 real NO_2 concentrations. Xu et al. (2013) have indicated that such overestimation was usually
136 significant in rural and remote areas but small at highly polluted urban sites with fresh
137 emissions, such as the study site in the present study. O_3 was measured by a commercial UV
138 photometric O_3 analyzer (*Model 49C, TEC, USA*) with a time resolution of 1 min. The

139 photolysis frequencies of NO_2 , HONO and O_3 (J_{NO_2} , J_{HONO} , J_{O_3}) were measured by a
140 CCD-detector spectrometer (*Metcon, Germany*), with a time resolution of 1 min. The fine
141 particle ($\text{PM}_{2.5}$ and $\text{PM}_{1.0}$) mass concentrations were continuously measured by a SHARP
142 Monitor (*Model 5030; Thermo Fisher Scientific, USA*). Beta rays attenuation and light
143 scattering photometry were used to quantify the hourly average particle concentrations. The
144 aerosol surface area density (S/V_a) was calculated from the particle number size distributions
145 between 5 nm and 10 μm , which were measured by a Wide-Range Particles Spectrometer
146 (*WPS, Model 1000XP, MSP Corporation, USA*), by assuming that the particles are in
147 spherical shape. The meteorological data including temperature, relative humidity (RH), and
148 wind speed and direction were measured with an automatic meteorological station
149 (*CAWS6000, China*) with a time resolution of 1 min. All of the above measurement
150 techniques have been successfully utilized in many previous studies (e.g., Wang et al., 2015;
151 Xue et al., 2011) .

152 3. Results and discussion

153 3.1. Data overview

154 Figure 2 shows an overview of the measured HONO, NO, NO_2 , $\text{PM}_{2.5}$, $\text{PM}_{1.0}$, J_{HONO} , and
155 meteorological parameters in the present study. During the 1-yr measurement period, the
156 prevailing winds were from the east and southwest sectors, indicating the general influence of
157 industrial emissions on the study site (see Fig. 1). The air temperature ranged from $-15\text{ }^\circ\text{C}$ to
158 $39\text{ }^\circ\text{C}$ with a mean value (\pm standard deviation) of $16\pm 11\text{ }^\circ\text{C}$, and the relative humidity showed
159 a clear seasonal variation pattern with higher levels in winter and summer. Markedly poor air
160 quality was observed as expected. Throughout the 1-yr period, 137 haze episodes occurred
161 with daily mass concentration of $\text{PM}_{2.5}$ exceeding the National Ambient Air Quality Standard
162 (Class II: $75\text{ }\mu\text{g m}^{-3}$), including 9 severe polluted haze episodes with daily average $\text{PM}_{2.5}$
163 concentrations above $250\text{ }\mu\text{g m}^{-3}$. In addition, elevated levels of NO_x , i.e., up to 350 ppbv of
164 NO and 108 ppbv of NO_2 , were also frequently recorded, possibly as a result of intensive
165 vehicle emissions nearby the study site. Overall, these observations highlight the nature of
166 our measurement station as a typical polluted urban environment in North China.

167 Table 1 documents the measured levels of HONO, NO_x, HONO/NO_x ratios and the
168 comparison with the results obtained previously elsewhere. The measured HONO mixing
169 ratios in Ji'nan ranged from 17 pptv to 8.36 ppbv with a mean (\pm SD) value of 1.15 ± 1.07 ppbv.
170 Elevated HONO concentrations were frequently observed during the measurement period,
171 with the daily maximum values exceeding 2 ppbv and 4 ppbv on 156 and 50 days,
172 respectively (see Fig. 2). The maximum hourly value of 7.39 ppbv was recorded in the early
173 morning of 6 December 2015. Such high levels of ambient HONO indicate the intense
174 sources of HONO and potentially strong atmospheric oxidizing capacity in urban Ji'nan. The
175 nighttime average (18:00-06:00, LT) HONO concentration was 1.28 ± 1.16 ppbv, compared to
176 the daytime average value (6:00-18:00, LT) of 0.99 ± 0.95 ppbv. In particular, the mean
177 HONO mixing ratio around noontime (11:00-13:00, LT) was even as high as 0.76 ± 0.61 ppbv,
178 which is nearly the highest levels ever recorded in the urban atmospheres, and about 27% of
179 the noontime HONO data were above 1.00 ppbv during the measurement period. This implies
180 the existence of strong daytime sources of HONO in the atmosphere of Ji'nan, which will be
181 further discussed in Section 3.4.

182 The seasonal variations of ambient HONO and related parameters are depicted in Fig. 3.
183 The highest concentrations of HONO occurred in winter (i.e., December–January), followed
184 by spring (i.e., April–May), summer (especially August) and autumn, with seasonal mean
185 (\pm SD) values of 1.71 ± 1.62 , 1.16 ± 0.90 , 1.12 ± 0.93 and 0.78 ± 0.60 ppbv, respectively. Overall,
186 the seasonal variation of HONO coincided with that of NO₂, an important precursor of
187 HONO. Such measured seasonal pattern of HONO is different from those measured in Hong
188 Kong (Xu et al., 2015) and Beijing (Hendrick et al., 2014), where the highest levels were
189 found in the autumn season. The wintertime peak of ambient HONO in Ji'nan should be the
190 result of the lower boundary layer height, weaker photolysis, and enhanced heterogeneous
191 production of HONO given the more abundant NO₂. The relatively higher springtime HONO
192 mixing ratios might be related to some degree to the more intense heterogeneous reactions of
193 NO₂ on the surface of mineral particles (Nie et al., 2012), as indicated by the coincident
194 higher concentrations of NO₂ and PM_{2.5} (note that PM₁₀ was not measured in the present
195 study). Indeed, the air quality of Ji'nan in the spring of 2016 was characterized by high levels

196 of particles and influenced by several dust storms and urban dust ([http://www.sdein.gov.cn](http://www.sdein.gov.cn/dtxx/hbyw/201605/t20160512_294758.html)
197 /dtxx/hbyw/201605/t20160512_294758.html). Besides, the elevated HONO levels in August
198 under the condition of intense solar radiation suggests the presence of strong HONO sources
199 as well as the important contributions of HONO as a potential source of OH radicals to the
200 atmospheric oxidation chemistry.

201 The diurnal profiles of HONO and related supporting parameters are shown in Figure 4.
202 Overall, the diurnal variations of HONO in different seasons were similar, which dropped
203 rapidly after sunrise and reached a minimum at around 15:00 LT, and then increased and
204 peaked during the morning rush hours (an exception is the winter case that showed a
205 concentration peak at midnight). The diurnal variation trend of HONO was similar to that of
206 NO, owing to a variety of chemical and physical processes, and the similar nighttime profiles
207 suggest that vehicle emissions may pose a significant effect on the measured HONO levels.
208 Such nighttime pattern was also found at Tung Chung, Hong Kong (Xu et al., 2015), a
209 roadside site in Houston, U.S. (Rappenglück et al., 2013) and in a tunnel in Wuppertal,
210 Germany (Kurtenbach et al., 2001). The average diurnal profiles of HONO/NO₂ ratio are also
211 shown in Fig. 4f. The HONO/NO₂ ratio generally decreased after sunrise due to the increase
212 of HONO photolysis, and then increased during the nighttime. An interesting finding was the
213 second peak of HONO/NO₂ at around noontime in spring, summer and winter seasons. If the
214 HONO sources during nighttime were the same as those at daytime, the minimum
215 HONO/NO₂ ratios should be found at noon due to the strong photolysis of HONO. Thus, the
216 higher ratios at noontime indicated the existence of additional daytime sources of HONO.
217 Moreover, the HONO/NO₂ ratios increased with solar radiation (e.g., J_{HONO}), implying that
218 the additional sources may be related to the solar radiation intensity. We will further discuss
219 the potential daytime sources of HONO in Section 3.4.

220 **3.2. Contribution of vehicle emissions**

221 As our study site is close to several major roads of large traffic fleet, it is necessary to
222 evaluate the contribution of vehicle emissions to the measured HONO concentrations. The
223 HONO/NO_x ratio was usually chosen to derive the emission factor of HONO in the freshly
224 emitted plumes (Kurtenbach et al., 2001). In order to ensure the fresh air masses, the

225 following four criteria were adopted to select the cases: (a) only data in the morning rush
226 hours (6:00-8:30 LT) in winter (e.g., November-February) were used; (b) $\text{NO}/\text{NO}_x > 0.7$; (c)
227 good correlation between HONO and NO_x ; (d) short duration of the plumes (<2 hours). Rush
228 hours are the prominent period with strong traffic emission and thus greatest contribution of
229 vehicle exhaust to HONO concentrations. Furthermore, during the winter early morning rush
230 hours when the solar radiation is weak and boundary layer height is relatively stable, the
231 derived HONO/ NO_x is less interfered by atmospheric photochemical reactions and mixing
232 with the air masses aloft. Criteria (b) was used as an indicator for identifying the freshly
233 emitted plumes. Criteria (c) and (d) further confirmed that the increase of HONO was mainly
234 attributed to direct emissions instead of heterogeneous reactions of NO_2 . The slopes of the
235 scatter plot of HONO versus NO_x can be considered as the emission ratios. With such strict
236 selection criteria, a total of twelve cases were screened out to estimate the vehicle emission
237 factors of HONO in urban Ji'nan.

238 Table 2 summarizes the estimated emission factors of HONO/ NO_x for the 12 vehicular
239 emission plumes. The average $\Delta\text{NO}/\Delta\text{NO}_x$ ratio of the selected plumes was 94%, indicating
240 that the air masses were indeed freshly emitted. The correlation coefficients (r^2) of HONO
241 with NO_x varied case by case and were in the range of 0.58-0.96, which may be due to the
242 inevitable mixing of vehicle plumes with other air masses and/or heterogeneous conversion
243 of NO_2 on soot particles and ground surface. The derived $\Delta\text{HONO}/\Delta\text{NO}_x$ ratios varied in the
244 range of 0.19%–0.87%, with an average value ($\pm\text{SD}$) of $0.53\% \pm 0.20\%$. This is comparable to
245 the emission factors obtained in Santiago, Chile (0.8%; Elshorbany et al., 2009) and
246 Wuppertal, Germany (0.3-0.8%; Kurtenbach et al., 2001), but is substantially lower than
247 those derived in Guangzhou (with a minimum value of 1.4%; Qin et al., 2009) and Houston,
248 U.S. (1.7%; Rappengluck et al., 2013). The emission factors should be dependent on the
249 types of vehicle engines, fuels and catalytic converters (Kurtenbach et al., 2001). The
250 variance in the HONO/ NO_x ratios derived from different metropolitan areas highlights the
251 necessity of examining the vehicular emission factors of HONO in the target city in the future
252 studies. In the present study, the average HONO/ NO_x value of 0.53% was adopted as the
253 emission factor in urban Ji'nan, and was used to estimate the contributions of traffic

254 emissions to the ambient nocturnal HONO levels (*Equation 1*) with a rough assumption that
255 the observed NO_x at our site was mainly emitted from vehicles.

$$256 \quad \text{HONO}_{\text{emis}} = \text{NO}_x \times 0.0053 \quad (\text{E1})$$

257 Where, HONO_{emis} is the HONO concentration arising from the direct vehicle emissions. The
258 calculated HONO_{emis} levels contributed on average 12%, 15%, 18% and 21% of the whole
259 measured nighttime HONO concentrations in urban Ji'nan in spring, summer, autumn and
260 winter, respectively.

261 **3.3 Heterogeneous conversion of NO₂ to HONO during nighttime**

262 It has been widely accepted that the heterogeneous reactions of NO₂ on wet surfaces
263 present an important formation pathway of ambient HONO, and generally make a dominant
264 contribution at nighttime (e.g., Finlayson-Pitts et al., 2003). To investigate the heterogeneous
265 production of HONO in Ji'nan, a number of nighttime HONO formation cases were
266 identified to estimate the NO₂-to-HONO conversion frequency. The selected cases should
267 meet the following criteria: (1) only the nighttime data in the absence of sunlight (i.e.,
268 20:00-05:59 LT in autumn and winter and 20:00-04:59 LT in spring and summer) were used
269 considering the fast HONO loss via photolysis and potential existence of unknown HONO
270 sources at daytime; (2) both HONO concentrations and HONO/NO₂ ratios increased steadily
271 during the target case; (3) the meteorological conditions, especially surface winds, should be
272 stable. Figure 5 presents an example of the heterogeneous HONO formation case occurring
273 on 6–7 September, 2015. In this case, the HONO mixing ratios increased rapidly after sunset
274 from 0.08 ppbv to 0.78 ppbv. Since the HONO concentrations and HONO/NO₂ almost
275 increased linearly throughout the night, the slope fitted by the least linear regression for
276 HONO/NO₂ ratios against time can be taken as the conversion frequency of NO₂-to-HONO
277 (k_{het} ; also referred to as C_{HONO} in other studies). During the 1-yr period, a total of 107 cases
278 were finally selected. Such a large set of cases facilitated a more robust statistical analysis of
279 the heterogeneous formation of HONO.

280 As our study site is close to the traffic roads, it is necessary to subtract the contribution
281 from direct vehicle emissions. The emission ratio of HONO/NO_x derived in Section 3.2 was

282 then used to adjust the HONO concentrations by *Eq. (2)*. The NO₂-to-HONO conversion
 283 frequency can be computed by *Eq. (3)*, by assuming that the increase of HONO/NO₂ ratio
 284 was caused by the heterogeneous conversion (Su et al., 2008a; Xu et al., 2015).

$$285 \quad \text{HONO}_{\text{corr}} = \text{HONO} - \text{NO}_x \times 0.0053 \quad (\text{E2})$$

$$286 \quad k_{\text{het}} = \frac{\frac{[\text{HONO}_{\text{corr}}](t_2) - [\text{HONO}_{\text{corr}}](t_1)}{[\text{NO}_2](t_2)} - \frac{[\text{HONO}_{\text{corr}}](t_2) - [\text{HONO}_{\text{corr}}](t_1)}{[\text{NO}_2](t_1)}}{(t_2 - t_1)} \quad (\text{E3})$$

287 The k_{het} values derived from the 107 cases showed a large variability, from 0.0013 h⁻¹ to
 288 0.0194 h⁻¹, with a mean value of 0.0068±0.0045 h⁻¹. These results are well within the range of
 289 k_{het} obtained previously from other urban areas. For example, the k_{het} in Ji'nan is comparable
 290 to that derived at an urban site of Shanghai (0.007 h⁻¹; Wang et al., 2013), and less than those
 291 in Guangzhou (0.016 h⁻¹; Qin et al., 2009), Milan (0.012 h⁻¹; Alicke et al., 2002) and
 292 Kathmandu (0.014 h⁻¹; Yu et al., 2009). Figure 6 provides the seasonal variation of the
 293 NO₂-to-HONO conversion rate in Ji'nan. Clearly, the largest average k_{het} was found in winter
 294 with a value of 0.0073±0.0044 h⁻¹. This should be ascribed to the higher S/V surface density
 295 within the shallower boundary layer in the wintertime. Moreover, weak correlation (R = 0.07)
 296 between k_{het} and aerosol surface density was also found, which suggests that the efficient
 297 heterogeneous formation of HONO may be independent on the aerosol surface.

298 The uptake coefficient of NO₂ on various surfaces to yield HONO ($\gamma_{\text{NO}_2 \rightarrow \text{HONO}}$) is a key
 299 parameter with large uncertainty in the air quality models to simulate HONO and OH radicals
 300 (Zhang et al., 2016). The overall $\gamma_{\text{NO}_2 \rightarrow \text{HONO}}$ on the bulk surface of ground and particles can
 301 be estimated from *Eq. (4)*.

$$302 \quad k_{\text{het}} = \gamma_{\text{NO}_2 \rightarrow \text{HONO}} \times c_{\text{NO}_2} \times \left(\frac{1}{4} \frac{S}{V_a} + \frac{1}{8} \frac{S}{V_g} \right) \quad (\text{E4})$$

$$303 \quad \frac{S}{V_g} = \frac{2.2}{H} \quad (\text{E5})$$

304 Where, c_{NO_2} is the mean molecular velocity of NO₂ (370 m s⁻¹); S/V_a and S/V_g are the
 305 surface area to volume ratio (m⁻¹) for both aerosol and ground, respectively. Considering the
 306 land use of the study site, the ground was treated as an uneven surface, and a factor of 2.2 per
 307 unit ground surface measured by Voogt and Oke (1997) was adopted to calculate the total

308 active surface. Hence, S/V_g can be calculated by *Eq. (5)*, where H is the mixing layer height
 309 and was obtained from the European Centre for Medium-Range Weather Forecasts
 310 (ECMRWF, ERA-Interim; <http://apps.ecmwf.int/datasets/data/interim-full-daily/levtype=sfc/>).
 311 The calculated uptake coefficients for the 107 cases varied in a wide range from 6.1×10^{-8} to
 312 1.7×10^{-5} , whilst the majority (5%-95% percentiles) fell in a narrower range of 1.1×10^{-7} to
 313 4.5×10^{-6} . The mean γ_{NO_2} value was $1.4 \pm 2.4 \times 10^{-6}$. Current laboratory studies have reported the
 314 range of $\gamma_{\text{NO}_2 \rightarrow \text{HONO}}$ from 10^{-6} to 10^{-5} on the ground surface (Kurtenbach et al., 2001;
 315 VandenBoer et al., 2013) and from 10^{-7} to 10^{-5} on the aerosol surface (Ndour et al., 2008;
 316 Wong et al., 2011). Obviously, the uptake coefficient in different orders of magnitude would
 317 definitely lead to different assessment of the importance of heterogeneous HONO sources (Li
 318 et al., 2010). The average uptake coefficient obtained from such a large set of samples could
 319 serve as a reference for modeling studies to simulate ambient HONO and atmospheric
 320 oxidation processes in the urban atmospheres of North China. Furthermore, the total area of
 321 ground surface is much larger than the reactive surface provided by aerosols, suggesting that
 322 the heterogeneous reactions of NO_2 on ground surface may play a dominant role. It should be
 323 noted that the exact uptake coefficients of NO_2 on ground and aerosol surfaces are variable
 324 and should be different, and the present analysis simplified this process by treating the
 325 ground and aerosol surfaces the same. Our derived uptake coefficients can be regarded as an
 326 equivalent γ_{NO_2} on the bulk surface of ground and particles.

327 3.4 Daytime HONO budget analysis

328 In this section, we examine the potential unknown source(s) of daytime HONO by a
 329 detailed budget analysis. *Equation (6)* summarizes the main factors affecting the ambient
 330 concentrations of HONO.

$$331 \quad \frac{d[\text{HONO}]}{dt} = P_{\text{emis}} + P_{\text{OH}+\text{NO}} + P_{\text{unknown}} - L_{\text{phot}} - L_{\text{OH}+\text{HONO}} - L_{\text{dep}} \quad (\text{E6})$$

332 Where, $d[\text{HONO}]/dt$ is the observed rate of change in the HONO mixing ratios; P_x terms
 333 indicate the sources of HONO, consisting of direct emission rate (P_{emis}), the gas phase
 334 formation rate ($P_{\text{OH}+\text{NO}}$, R2), and the unknown HONO daytime source (P_{unknown}); L_y terms
 335 denote the sink processes, including the photolysis rate (L_{phot} , R1), reaction rate of HONO

336 with OH ($L_{OH+HONO}$, R5), and dry deposition rate (L_{dep}). Here we omitted the influence of
 337 vertical and horizontal transport since their contributions to ambient HONO are far less than
 338 photolysis and gas phase reactions at noontime. The average daytime wind speed in Ji'nan in
 339 the present study was 1.7 m s^{-1} , so that at a HONO lifetime of about 15 min at noontime, the
 340 horizontal transport had to occur within 1.6 km (in which no large-scale pollution sources) to
 341 reach the site. Dillon et al. (2002) proposed a parameterization for the dilution by background
 342 air to estimate the magnitude of vertical transport ($T_V = k_{\text{(dilution)}}([\text{HONO}] - [\text{HONO}]_{\text{background}})$).
 343 Even though taking a mean noontime [HONO] level of 1 ppbv, a value of $6 \times 10^{-5} \text{ ppb s}^{-1}$ was
 344 derived (Dillon et al., 2002; Sörgel et al., 2011), which is much smaller compared to L_{phot}
 345 ($1 \times 10^{-3} \text{ ppb s}^{-1}$).

346 The noontime data (11:00-14:00 LT) with the strongest solar radiation were chosen to
 347 calculate the unknown HONO source strength based on Eq. (7). Here the $d[\text{HONO}]/dt$ was
 348 approximated by $\Delta\text{HONO}/\Delta t$, which is the difference of the measured HONO concentrations
 349 every 10 minutes (Sörgel et al., 2011).

$$350 \quad P_{\text{unknown}} = L_{\text{phot}} + L_{\text{OH+HONO}} + L_{\text{dep}} + \frac{\Delta[\text{HONO}]}{\Delta t} - P_{\text{OH+NO}} - P_{\text{emis}} \quad (\text{E7})$$

$$351 \quad = [\text{HONO}] \left(J_{\text{HONO}} + K_{\text{OH+HONO}}[\text{OH}] + \frac{\vartheta_{\text{HONO}}^{\text{ground}}}{H} \right) + \frac{\Delta[\text{HONO}]}{\Delta t} - K_{\text{OH+NO}}[\text{OH}][\text{NO}] -$$

$$352 \quad \frac{\Delta[\text{NO}_x] \times 0.54\%}{\Delta t}$$

$$353 \quad [\text{OH}] = a(J_{\text{O}^1\text{D}})^\alpha (J_{\text{NO}_2})^\beta \frac{b\text{NO}_2+1}{c\text{NO}_2^2+d\text{NO}_2+1} \quad (\text{E8})$$

$$354 \quad (\alpha = 0.83, \beta = 0.19, a = 4.1 \times 10^9, b = 140, c = 0.41, \text{ and } d = 1.7)$$

355 Where, J_{HONO} and J_{NO_2} are the photolysis frequencies of HONO and NO_2 (s^{-1}), respectively.
 356 Direct measurements of J_{HONO} and J_{NO_2} were made in this study except for the period from
 357 December 2015 to May 2016. For the reaction of HONO with OH, a rate constant $K_{\text{OH+HONO}}$
 358 of $6.0 \times 10^{-12} \text{ cm}^3 \text{ molecules s}^{-1}$ was taken from Atkinson et al. (2004). The OH mixing ratios
 359 were expressed by the NO_2 concentrations and photolysis frequencies of O_3 and NO_2 , as
 360 shown in Eq. (8) (Alicke et al., 2002). In the present study, the calculated daily peak OH
 361 concentrations were in the range of $0.3\text{-}2 \times 10^7 \text{ molecules cm}^{-3}$, which are comparable to those

362 measured in the polluted atmospheres of northern China (Lu et al., 2013). Nonetheless, it
363 should be noted that the OH calculation from such empirical equation may be subject to some
364 uncertainty. L_{dep} was calculated by assuming a HONO daytime dry deposition velocity of 2
365 cm s^{-1} and an effective mixing height of 200 m. Due to the rapid photolysis of HONO at
366 daytime, most of HONO cannot reach the height above 200 m (Alicke et al., 2002). K_{OH+NO}
367 is the rate constant for the reaction of OH with NO, using a value of $9.8 \times 10^{-12} \text{ cm}^3$
368 $\text{molecules}^{-1} \text{ s}^{-1}$ from (Atkinson et al., 2004). The emission source strength was estimated from
369 the HONO/NO_x emission ratio of 0.53% as determined in Sec. 3.2.

370 Figure 7 shows the average contributions of all the source and sink terms to the HONO
371 budget in August 2016, when accurate J values observations were available and elevated
372 daytime HONO were observed. An unknown source $P_{unknown}$ was clearly the dominant part,
373 accounting for over 80% of the HONO production. An average $P_{unknown}$ value of 2.95 ppb h^{-1}
374 was derived, which is more than 7 times greater than that of the homogeneous formation rate
375 (P_{OH+NO} , 0.40 ppb h^{-1}). The major loss pathway of HONO was the photolysis with a mean
376 L_{phot} value of 2.80 ppb h^{-1} , followed by dry deposition (L_{dep} , 0.49 ppb h^{-1}), and $L_{OH+HONO}$
377 was very small and almost less than 3% of L_{phot} . The unknown source strength of daytime
378 HONO in Ji'nan is higher than those derived in Santiago, Chile (1.69 ppb h^{-1} ; Elshorbany et
379 al., 2009), Beijing (1.83 ppb h^{-1} ; Hou et al., 2016), and Houston, US (0.61 ppb h^{-1} ; Wong et
380 al., 2012). Some studies have reported much lower $P_{unknown}$ obtained from a rural site in
381 Guangzhou, China (0.76 ppb h^{-1} ; Li et al., 2012), a mountain site in Hohenpeissenberg,
382 Germany (0.40 ppb h^{-1} ; Acker et al., 2006), and a forest site in Julich, Germany (0.50 ppb h^{-1} ;
383 Kleffmann et al., 2005).

384 We further explored the potential unknown daytime source(s) of HONO based on our
385 measurement data. According to the laboratory studies, heterogeneous reactions of NO₂ on
386 wet surfaces should be an important contributor to the ambient HONO concentrations, and
387 the reaction rate is first order in NO₂. It has been also proposed that these heterogeneous
388 reactions can be photo-enhanced (Stemmler et al., 2006). Thus, the strength of the unknown
389 HONO source ($P_{unknown}$) can be expressed by equation (E9), if the heterogeneous reactions
390 were the major HONO sources.

$$P_{unknown} \propto J_{NO_2} * [NO_2] * \left[\frac{S}{V} \right] \quad (E9)$$

Correlation analysis between $P_{unknown}$ and related parameters has been widely adopted to diagnose the potential HONO sources (e.g., Su et al., 2008b). The NO_2 concentration ($[NO_2]$) is usually used as an indicator of the heterogeneous reactions on the ground surface since the ground surface to volume ratio (S/V_g) can be assumed to be constant for the well-mixed boundary layer at noontime, whilst $[NO_2]*[S/V_a]$ can be taken as a proxy for the HONO formation on the aerosol surface. $J_{NO_2}*[NO_2]$ and $J_{NO_2}*[NO_2]*[S/V_a]$ can be used to infer the photo-enhanced heterogeneous reactions on ground and aerosol surfaces. Figure 8 shows the scatter plots of the calculated $P_{unknown}$ versus the abovementioned four indicators for the summer case (i.e., August 2016) when accurate J value measurements were available. $P_{unknown}$ showed a moderate correlation with $[NO_2]$ with a correlation coefficient (R) of 0.55, and it was significantly improved after $J_{NO_2}*[NO_2]$ was considered (R=0.76). When aerosol surface density was taken into account, however, the correlation became even weaker with R values of 0.40 and 0.43. This suggests that the photo-enhanced heterogeneous reactions of NO_2 on the ground surface played a major role in the daytime HONO formation in Ji'nan in summer.

3.5 Impact on the primary OH sources

Photolysis of HONO presents an important primary source of OH in the atmosphere. The elevated levels of daytime HONO imply a sufficient supply of OH radicals and hence strong atmospheric oxidizing capacity in the urban atmosphere of Ji'nan. Here we assessed the contribution of HONO photolysis to the OH production and compared against that from O_3 photolysis (O^1D+H_2O), another important OH source, based on the concurrent observations of HONO, O_3 , J_{HONO} and J_{O1D} in summer. The other primary OH sources, such as photolysis of peroxides and ozonolysis reactions of alkenes, are generally not very important in urban areas, especially at daytime, and were not considered in the present study. We also don't consider the primary sources of HO_2 and RO_2 radicals (such as photolysis of OVOCs) due to the lack of measurement data for these radical precursors. The net OH production rate from HONO photolysis ($P_{OH}(HONO)_{net}$) was calculated by the source strength subtracting the sink terms due to reactions (R2) and (R5) (Equations 10 and 11). The OH production rate

419 from O_3 photolysis can be calculated by *Equation (12)* (Su et al., 2008b).

$$420 \quad P_{OH}(HONO) = J_{HONO} \times [HONO] \quad (E10)$$

$$421 \quad P_{OH}(HONO)_{net} = P_{OH}(HONO) - k_{NO+OH}[NO][OH] - k_{HONO+OH}[HONO][OH] \quad (E11)$$

$$422 \quad P_{OH}(O_3) = 2J_{O^1D} \times [O_3] / (1 + k_3[M]/k_2[H_2O]) \quad (E12)$$

423 Figure 9 shows the daytime profiles of OH production rates from photolysis of HONO
 424 and O_3 in the summer (i.e., August 2016) period when accurate J value measurements were
 425 available. Clearly, photolysis of HONO dominated the daytime OH production in urban
 426 Ji'nan. The mean $P_{OH}(HONO)$ was 1.88 ppb h^{-1} , almost 3 times higher than $P_{OH}(O_3)$.
 427 Furthermore, in contrast to most of the earlier studies which suggested that the contribution
 428 of HONO photolysis was mainly concentrated in the early morning and neglected at noon,
 429 photolysis of HONO presents the dominant OH contributor throughout the daytime at our
 430 study site. Even though at noontime in summer, high contributions of HONO photolysis were
 431 still found. These results demonstrate the significant role of HONO in the atmospheric
 432 oxidizing capacity in the urban atmosphere of Ji'nan.

433 **4. Summary**

434 Highly time-resolved continuous field observations of HONO, related air pollutants and
 435 meteorological parameters were performed at an urban site of Ji'nan in North China, for a
 436 year from September 2015 to August 2016. The measured mean concentration of HONO was
 437 1.15 ppbv with a maximum level of 8.36 ppbv . The ambient HONO concentrations presented
 438 a seasonal variation with the highest level in winter as well as elevated concentrations in
 439 spring (April-May) and summer (August). Well-defined diurnal cycles of HONO with
 440 concentration peaks in the early morning and valleys in the afternoon were found for all the
 441 four seasons. Direct emissions from vehicle exhaust posed a large contribution to the ambient
 442 HONO, with an average emission ratio $\Delta HONO/\Delta NO_x$ of 0.53%. During the nighttime, the
 443 heterogeneous conversion of NO_2 on the ground surface is an important source of HONO.
 444 The average conversion frequency of NO_2 to HONO was derived as 0.0068 h^{-1} from over
 445 hundred cases. At daytime, a missing HONO source with an average strength of 2.95 ppb h^{-1}
 446 was derived in summer, which was about seven times larger than the gas phase reactions. Our

447 analysis implied that the photo-enhanced heterogeneous reaction of NO₂ on the ground
448 surface may be a major source of daytime HONO in summer. Photolysis of HONO presents
449 the predominant OH contributor not only in the early morning but also throughout the
450 daytime in urban Ji'nan, and hence plays a vital role in the atmospheric oxidation and ozone
451 formation in the polluted urban atmosphere of northern China.

452 **Acknowledgments**

453 We thank Chuan Yu, Ruihan Zong, Dr. Zheng Xu and Dr. Long Jia for their contributions
454 to the field study. We are grateful to the European Centre for Medium-Range Weather
455 Forecasts for sharing the boundary layer height data and to the National Center Atmospheric
456 Research for providing the TUV model. This work was funded by the National Natural
457 Science Foundation of China (No. 41505111 and 91544213), the National Key Research and
458 Development Programme of the Ministry of Science and Technology of China (No.
459 2016YFC0200500), the Natural Science Foundation of Shandong Province (ZR2014BQ031),
460 the Qilu Youth Talent Program of Shandong University, and the Jiangsu Collaborative
461 Innovation Center for Climate Change.

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Table 1. Overview of the measured HONO and NO_x levels in urban Ji'nan and comparison with other studies.

Location	Time	HONO(ppb)		NO ₂ (ppb)		NO _x (ppb)		HONO/NO ₂		HONO/NO _x		Ref.
		N	D	N	D	N	D	N	D	N	D	
Santiago, Chile (urban)	Mar-Jun 2005	3.00	1.50	30.0	20.0	200.0	40.0	0.100	0.075	0.015	0.038	1
Rome, Italy (urban)	May-Jun 2001	1.00	0.15	27.2	4.0	51.2	4.2	0.037	0.038	0.020	0.024	2
Kathmandu, Nepal (urban)	Jan-Feb 2003	1.74	0.35	17.9	8.6	20.1	13.0	0.097	0.041	0.087	0.027	3
Shanghai, China (urban)	Oct 2009	1.50	1.00	41.9	30.0	/	/	0.038	0.032	/	/	4
Guangzhou, China (urban)	Jun 2006	3.5	2.00	20.0	30.0	/	/	0.175	0.067	/	/	5
Beijing, China (urban)	Oct-Nov 2014	1.75	0.93	37.6	35.3.0	94.5	53.4	0.047	0.026	0.019	0.017	6
Xinken, China (suburban)	Oct-Nov 2004	1.30	0.80	34.8	30.0	37.8	40.0	0.037	0.027	0.034	0.020	7
Milan, Italy (suburban)	May-Jun 1998	0.92	0.14	33.2	18.3	117.5	23.4	0.028	0.008	0.008	0.006	8
Backgarden, China (rural)	Jul 2006	0.95	0.24	16.5	4.5	20.9	5.5	0.057	0.053	0.045	0.043	9
	Sep 2015-Aug 2016	1.28	0.99	31.0	25.8	46.4	40.6	0.079	0.056	0.040	0.035	10
	Sep-Nov 2015 (autumn)	0.87	0.66	25.4	23.2	38.	37.5	0.049	0.034	0.034	0.022	10
Ji'nan, China (urban)	Dec 2015-Feb 2016 (winter)	2.15	1.35	41.1	34.6	78.5	64.8	0.056	0.047	0.034	0.031	10
	Mar-May 2016 (spring)	1.24	1.04	35.8	25.8	47.3	36.0	0.046	0.052	0.035	0.041	10
	Jun-Aug 2016 (summer)	1.20	1.01	22.5	19.0	29.1	25.8	0.106	0.079	0.060	0.049	10

N: nighttime (18:00-06:00, LT); D: daytime (06:00-18:00, LT)

1: Elshorbany et al. (2009); 2: Acker et al. (2006a); 3: Yu et al. (2009); 4: Bernard et al. (2016); 5: Qin et al. (2009); 6: Tong et al. (2015); 7: Su et al. (2008a); 8: Alicke et al. (2002); 9: Li et al. (2012); 10: this study.

Table 2. The emission ratios $\Delta\text{HONO}/\Delta\text{NO}_x$ of fresh vehicle plumes.

Date	Local Time	$\Delta\text{NO}/\Delta\text{NO}_x$	R^2	$\Delta\text{HONO}/\Delta\text{NO}_x$ (%)
11/03/2015	06:08-07:45	0.89	0.91	0.29
11/05/2015	06:00-07:30	0.92	0.84	0.63
11/17/2015	06:00-07:30	1	0.95	0.75
11/20/2015	06:00-07:15	0.92	0.72	0.59
12/06/2015	06:00-07:48	0.83	0.75	0.87
12/08/2015	06:02-07:30	0.95	0.61	0.58
12/25/2015	06:00-07:30	0.94	0.72	0.30
12/31/2015	06:00-07:30	0.96	0.94	0.47
01/02/2016	06:00-07:30	1	0.61	0.46
01/20/2016	06:44-07:48	0.92	0.96	0.71
01/21/2016	06:26-07:56	0.94	0.58	0.54
01/27/2016	07:00-08:12	0.89	0.77	0.19

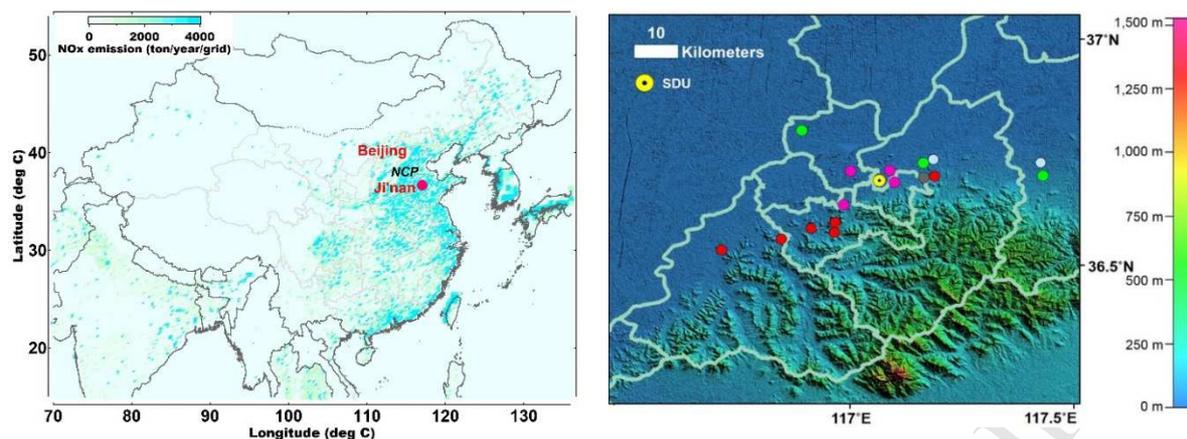


Figure 1. Locations of Ji'nan and the sampling site. The left map is color-coded by the anthropogenic NO_x emissions (Zhang et al., 2009), while the right is color-coded by the geographical height. The large industrial sources are labeled with different colors, including steel plants (light blue), thermal power plants (pink), cement plants (red), oil refineries (grey) and chemical plants (green).

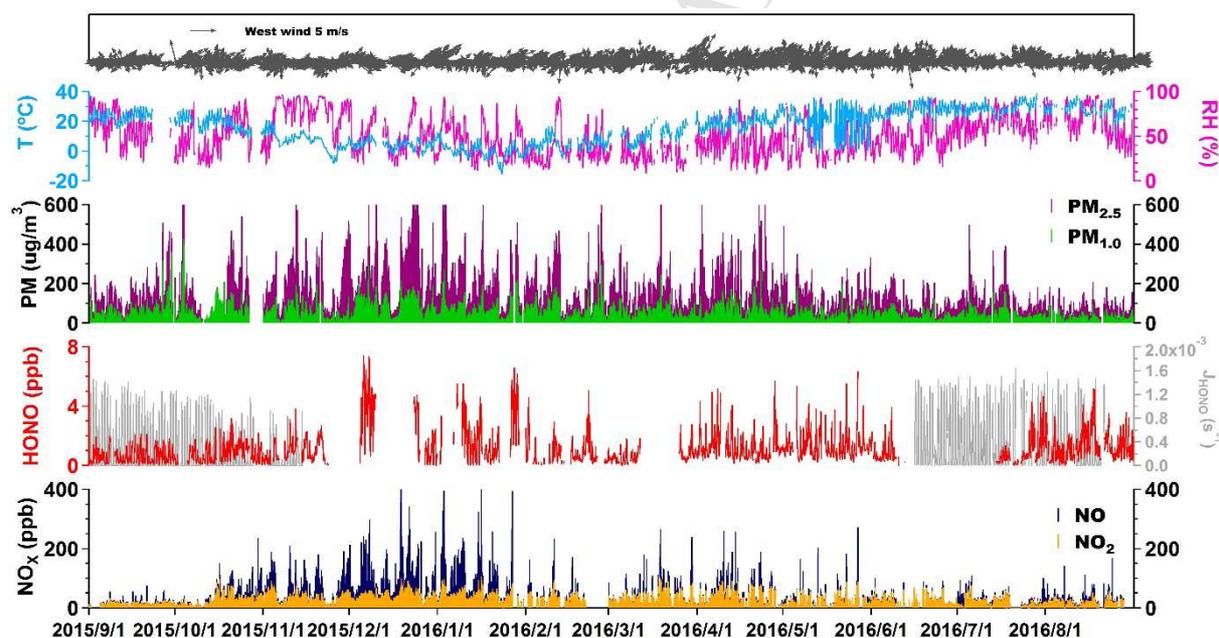


Figure 2. Time series of HONO, NO, NO₂, PM_{2.5}, PM_{1.0}, J_{HONO}, temperature (T), relative humidity (RH) and surface wind in Ji'nan from September 2015 to August 2016. The data gap is mainly due to the maintenance of the instruments.

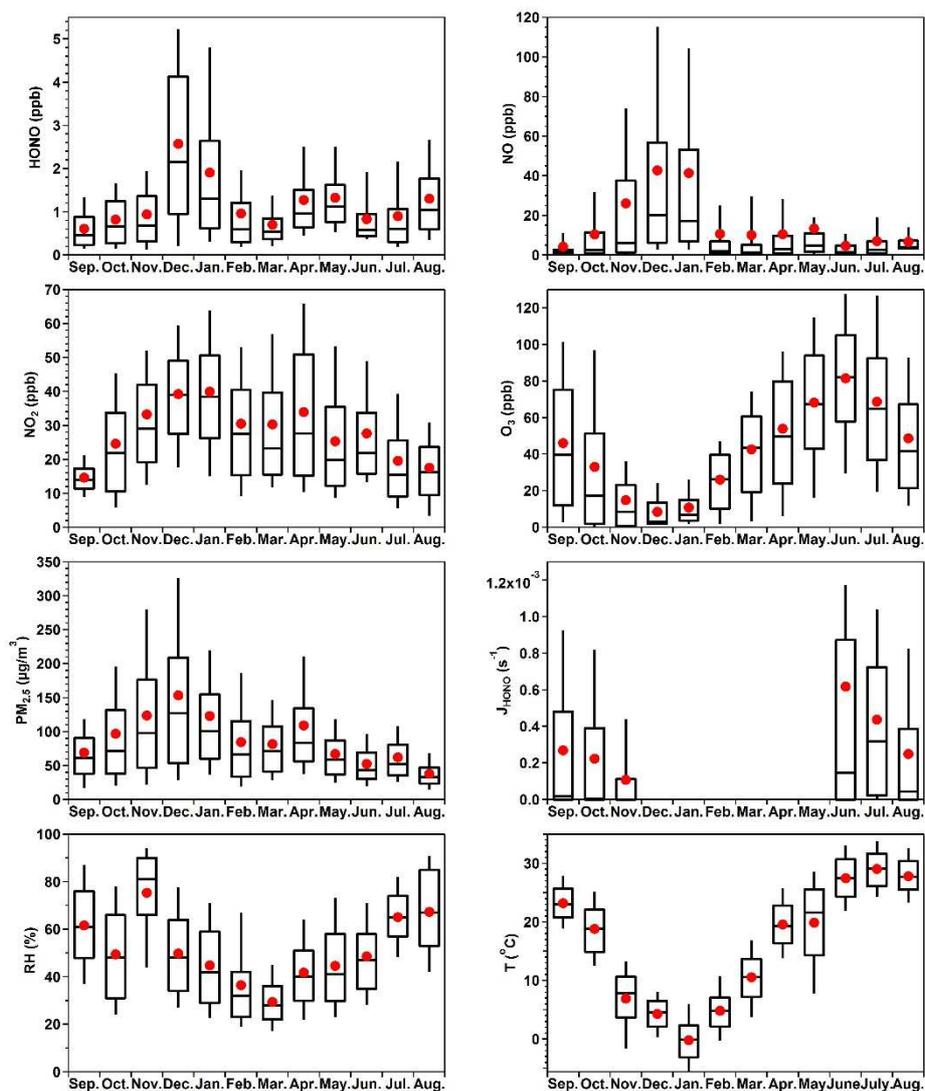


Figure 3. Seasonal variations of HONO, NO, NO₂, O₃, PM_{2.5}, J_{HONO} and RH and T. The box plot provides the 10%, 25%, 50%, 75% and 90% the data, while the red dots indicate the average concentrations.

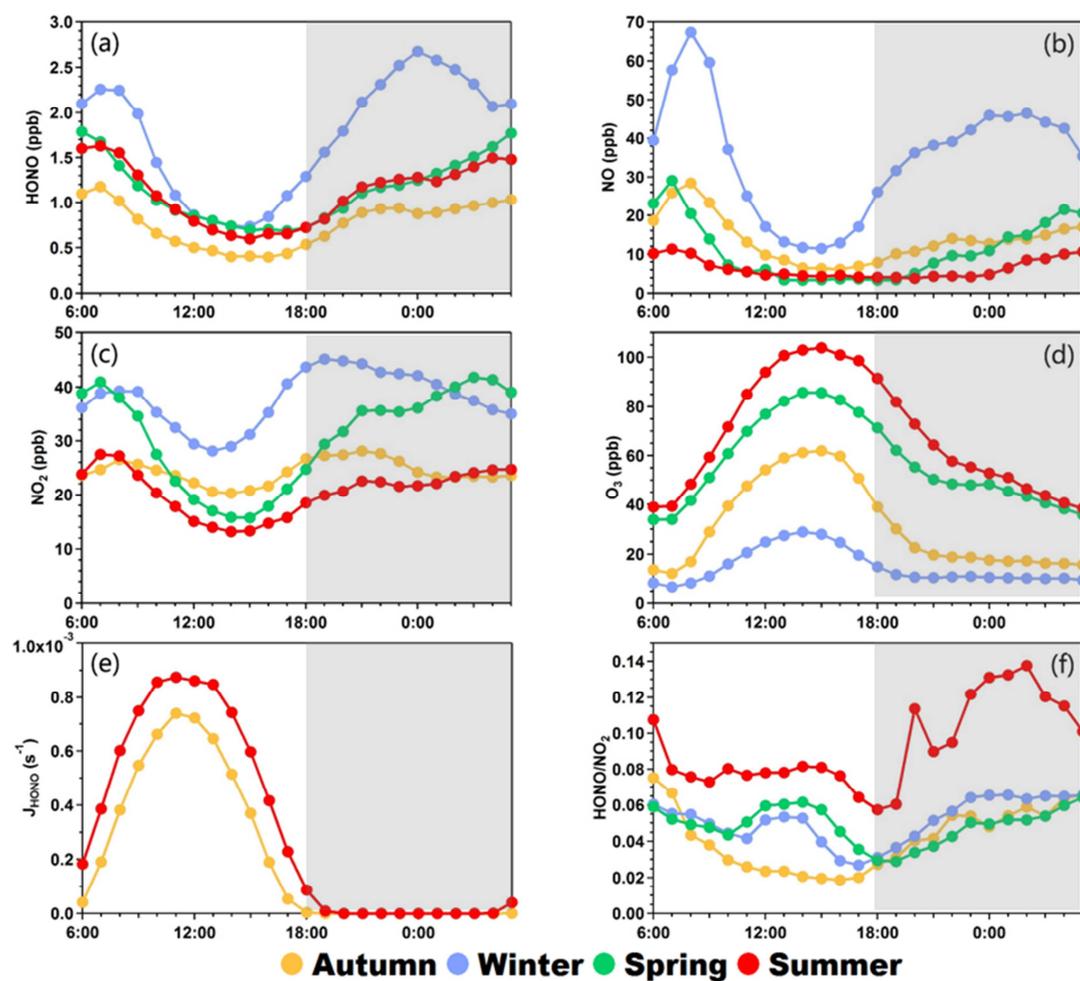


Figure 4. Diurnal variations of (a) HONO, (b) NO, (c) NO₂, (d) O₃, (e) J_{HONO}, and (f) HONO/NO₂ in the four seasons. The grey shaded area indicates the nighttime period (18:00-06:00 LT; note that the exact nighttime periods varied with different seasons).

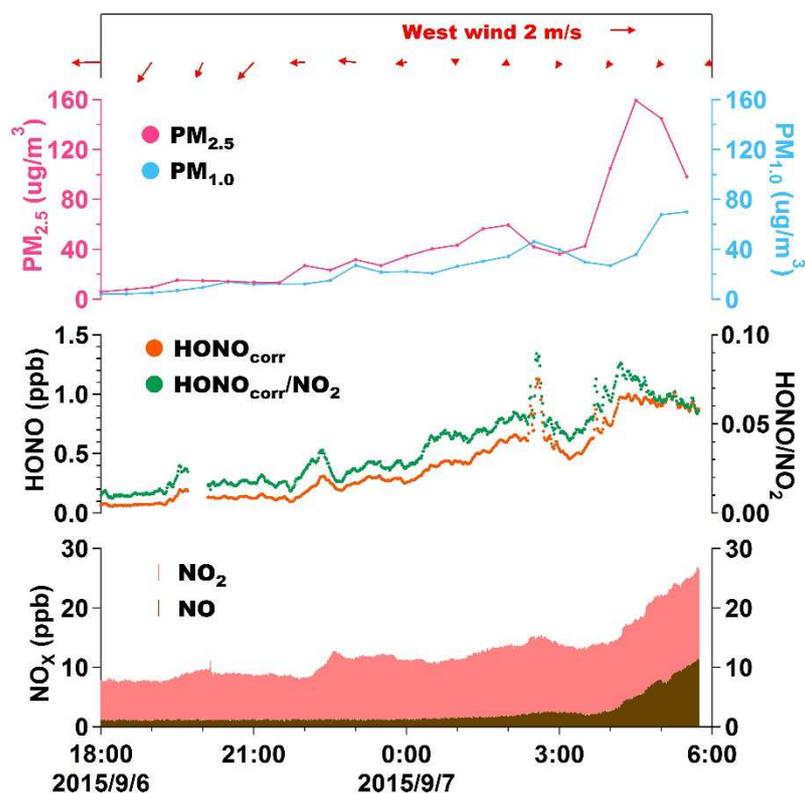


Figure 5. A case of the determination of heterogeneous NO_2 -to-HONO conversion frequency at nighttime.

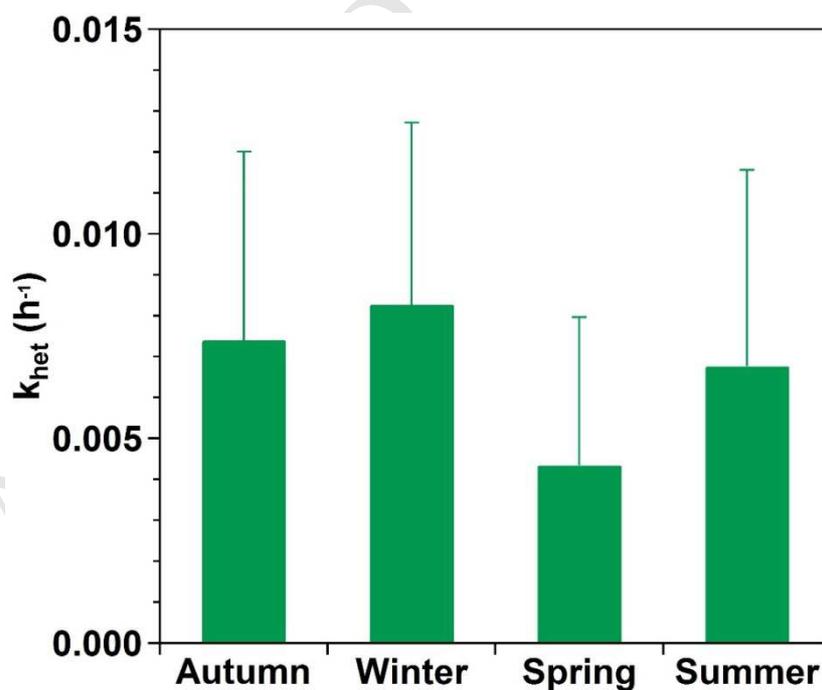


Figure 6. Seasonal variation of the NO_2 -to-HONO conversion frequency (k_{het}) in Ji'nan.

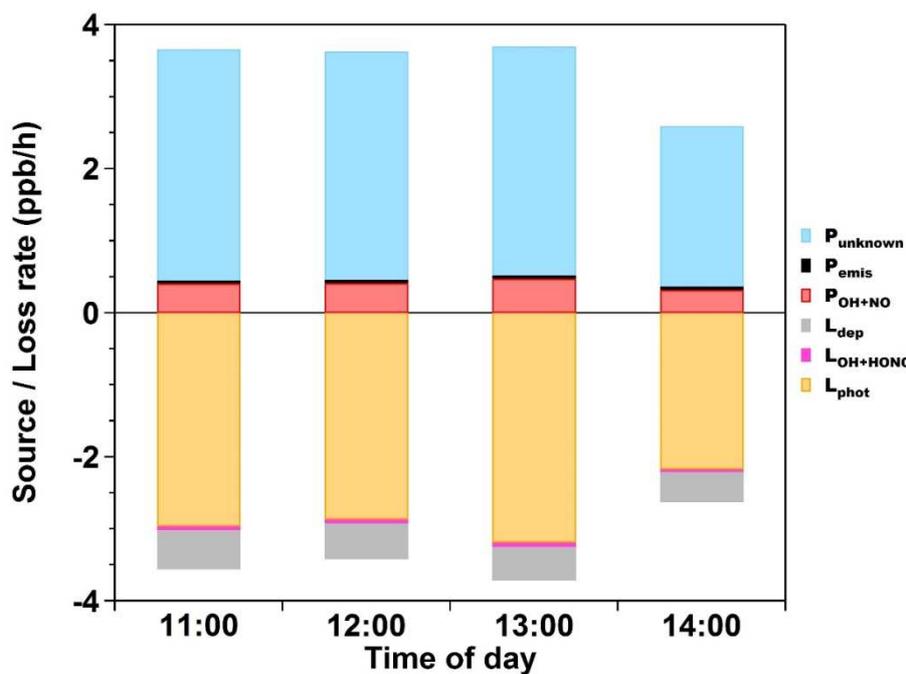


Figure 7. Average daytime HONO budget at noon (11:00-14:00 LT) in August 2016.

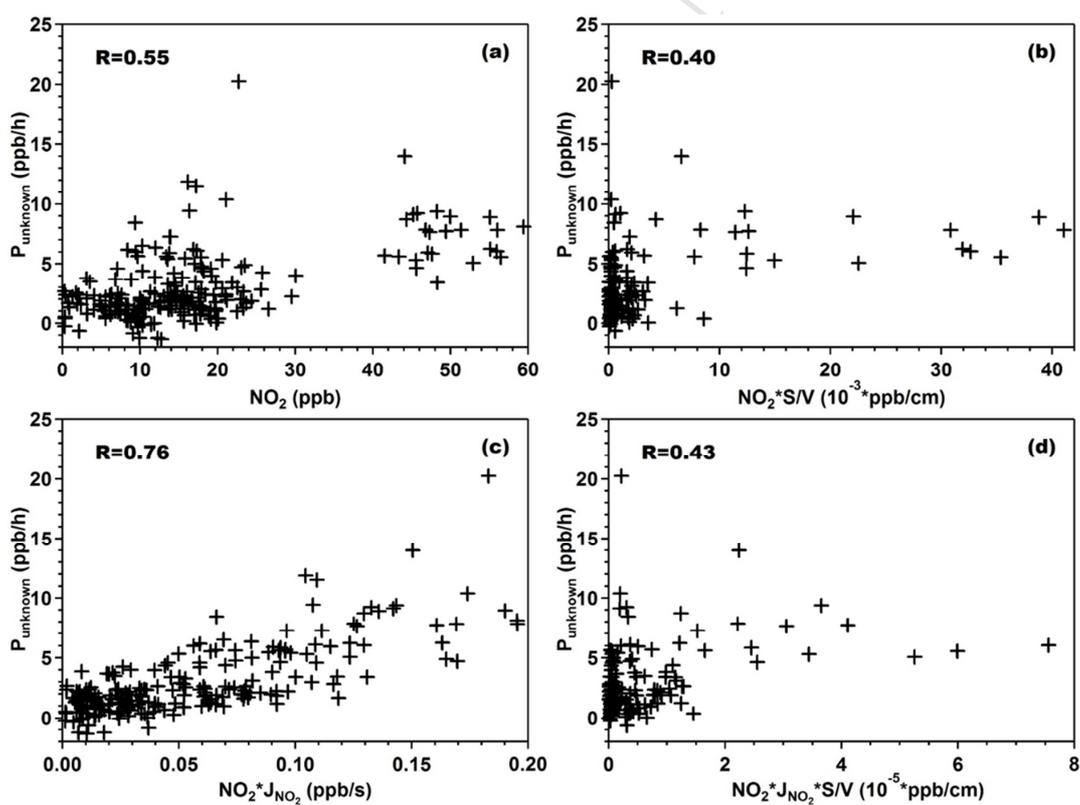


Figure 8. Scatter plots of the unknown daytime HONO source strength (P_{unknown}) with (a) NO_2 , (b) $\text{NO}_2 \cdot (\text{S}/\text{V})_a$, (c) $\text{NO}_2 \cdot J_{\text{NO}_2}$, and (d) $\text{NO}_2 \cdot J_{\text{NO}_2} \cdot (\text{S}/\text{V})_a$ during August 2016.

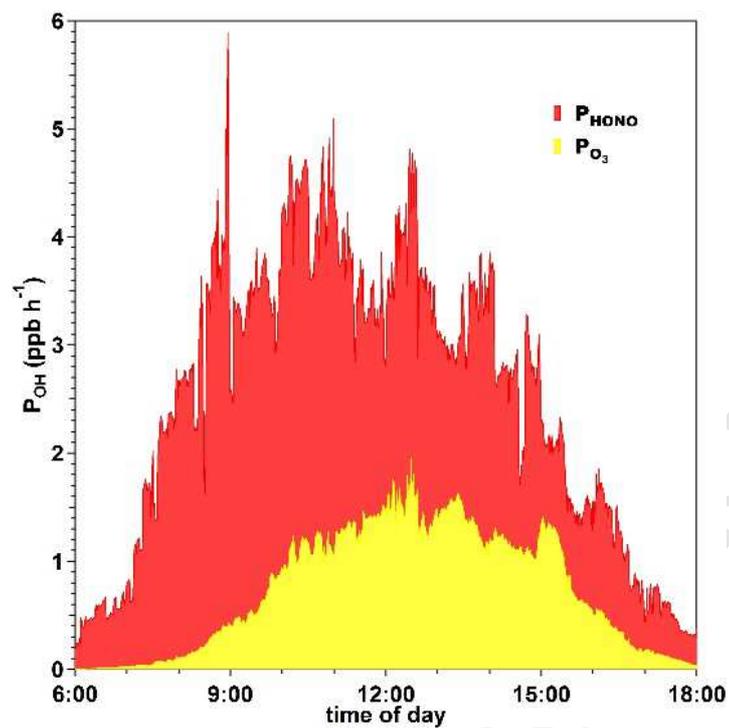


Figure 9. Average OH production rates from photolysis of HONO and O₃ in summer (August 2016).

Highlights:

- One-year continuous measurements of HONO were made at a typical urban site in northern China.
- Seasonal and diurnal variations, vehicle emission factors, heterogeneous formation, and daytime sources were examined based on a large observational data set.
- A strong missing daytime source was needed to explain the measured HONO concentrations.
- HONO photolysis is the dominant OH source throughout the daytime.