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1 HONO budget and its role in nitrate 2 formation in the rural North China Plain

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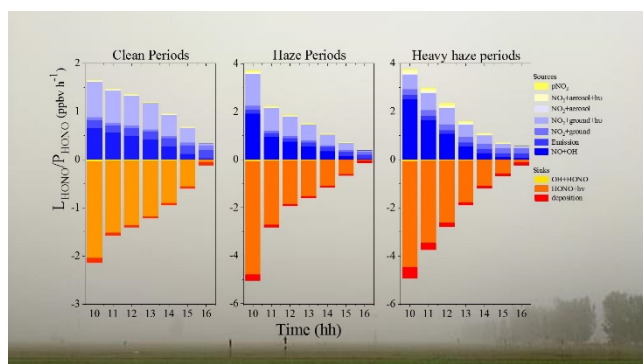
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34 TOC Art



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36

37 Abstract

38 Nitrous acid (HONO) is a major precursor of tropospheric hydroxyl radical (OH) that accelerates
39 the formation of secondary pollutants. The HONO sources, however, are not well understood,
40 especially in polluted areas. Based on a comprehensive winter field campaign conducted at a rural
41 site of the North China Plain, a box model (MCM v3.3.1) was used to simulate the daytime HONO
42 budget and nitrate formation. We found that HONO photolysis acted as the dominant source for
43 primary OH with a contribution of more than 92%. The observed daytime HONO could be well
44 explained by the known sources in the model. The heterogeneous conversion of NO₂ on ground
45 surfaces and the homogeneous reaction of NO with OH were the dominant HONO sources with
46 contributions of more than 36% and 34% to daytime HONO, respectively. The contribution from
47 the photolysis of particle nitrate and the reactions of NO₂ on aerosol surfaces were found to be
48 negligible in clean periods (2%) and slightly higher during polluted periods (8%). The relatively
49 high OH levels due to fast HONO photolysis at the rural site remarkably accelerated gas-phase
50 reactions, resulting in the fast formation of nitrate as well as other secondary pollutants in the
51 daytime.

52 Introduction

53 The hydroxyl radical (OH) is the most important oxidant in the troposphere to initiate the oxidation
54 of organic and inorganic compounds, leading to the formation of secondary pollutants such as ozone
55 (O₃), secondary organic (SOA) and secondary inorganic aerosols (SIA), which deteriorate regional
56 air quality^{1,2}. Therefore, numerous field campaigns over the world have been conducted with the
57 target to improve our understanding of radical chemistry, including the quantification of the sources
58 and sinks of OH^{1,2}. Nitrous acid (HONO) has been recognized as an important primary OH source
59 to initiate daytime atmospheric photochemistry³. Recent studies found that HONO not only played
60 a dominant role in triggering daytime atmospheric chemistry in the early morning but also acted as
61 an important, even the dominant OH source throughout the whole day, e.g., the photolysis of HONO
62 contributed ca. 20%-80% of atmospheric primary OH production in polluted regions⁴⁻⁸. Because
63 the classic gas-phase reaction of NO with OH cannot explain the extremely high HONO levels

64 observed in the daytime, additional HONO sources were further proposed based on laboratory
65 studies and field campaigns including a) direct emission from combustion process⁹⁻¹³, b) NO₂
66 heterogeneous reduction on various surfaces such as soil^{14,15}, c) photosensitized NO₂ heterogeneous
67 reduction on the organic surfaces^{16,17}, d) photolysis of total nitrate (TNO₃, the sum of nitric acid
68 (HNO₃) and particle nitrate (pNO₃))¹⁸⁻²⁰, e) soil abiotic or biotic emissions^{21,22} and f) other proposed
69 HONO sources²³. A detailed summary of HONO sources can be found in the Supplementary
70 Information (SI). Several studies evaluated the relative contribution of each source to atmospheric
71 HONO through the comparison between model simulations and the observations, indicating that
72 atmospheric HONO in the daytime still could not be well explained in many polluted areas²⁴⁻²⁷.
73 The North China Plain (NCP) is suffering from severe particle/aerosol pollution (usually called haze
74 pollution), especially in wintertime, and extremely high HONO concentrations were also frequently
75 observed during the winter haze pollution events in the NCP^{28,29}. For example, Li et al.²⁸ reported
76 an averaged noontime HONO mixing ratio of up to ca. 1.0 ppbv under high particle concentrations
77 in Ji'nan city (China). Zhang et al.²⁹ found maximum and noontime HONO mixing ratios of 10.7
78 ppbv and ca. 1.4 ppbv during haze pollution periods in the winter of Beijing, respectively. However,
79 modeled and measured HONO levels were still not in agreement, e.g., noontime HONO levels in
80 winter of Beijing were still underestimated by 50% even if the HONO sources of direct emission,
81 NO₂ heterogeneous reactions, and soil emission were taken into account in WRF-Chem models^{26,27}.
82 Particle nitrate in the winter of the NCP was recently found to be the major inorganic aerosol
83 component with contribution comparable to or even larger than sulfate and showed a still increasing
84 trend during the last decade³⁰. Recent laboratory studies reported that photolysis of particle nitrate
85 could lead to significant production of HONO with photolysis rates 2-3 orders of magnitude
86 faster^{18,19} than the photolysis of pure HNO₃ in the gas phase or adsorbed on clean glass surfaces³¹.
87 In contrast, Romer et al.³² found that only moderate enhancements of 1-30 times faster are most
88 consistent with the observations. Therefore, the exceptionally high concentration of particle nitrate
89 during the haze period in winter of the NCP may also make a potential contribution to atmospheric
90 HONO. However, up to now, no study evaluates the contribution of particle nitrate photolysis to
91 atmospheric HONO in the NCP. Additionally, the high levels of daytime HONO during winter haze
92 days in the NCP would significantly contribute to OH radicals that promote particle nitrate
93 formation through the reaction of NO₂ with OH³³, whereas, the quantification of the contribution of
94 HONO to OH and nitrate formation under haze conditions in the NCP is rarely reported^{6,8}.
95 In the present work, based on a comprehensive field campaign with measurements of various
96 pollutants (HONO, VOCs, aerosols, etc.) and meteorological parameters during winter at a rural site
97 of the NCP, a box model (MCM v3.3.1) was used to explore the HONO budget concerning the
98 reported sources (i.e., homogeneous reaction, direct emission, NO₂ reduction on aerosol and ground
99 surfaces, and particle nitrate photolysis) and its contribution to radical and nitrate formation.

100 **Methods**

101 **Field measurements**

102 Field observation of HONO and related pollutants were conducted at the station of Rural
103 Environmental, Chinese Academy of Sciences (SRE-CAS), located in Dongbaituo village (38°42'N,

104 115°15'E), Hebei province, China. The station was surrounded by agricultural fields planted with
105 winter wheat. It's about 30 km in the southwest of Baoding city and 170 km to the southwest of
106 Beijing. The nearest county seat, Wangdu, is about 10 km northwest to the station. The detailed
107 information about the station has been well documented in our previous studies³⁴. During the
108 campaign from 3rd to 24th in December of 2017, a commercial LOPAP (QUMA, Model LOPAP-03)
109 was used to measured HONO concentrations^{35,36}. Instrument background signals were conducted
110 by sampling ultrapure nitrogen at least twice per day, and single-point calibrations were carried out
111 by diluted nitrite standard solution (Sigma-Aldrich) at least once per week. Intercomparison in the
112 NCP between various HONO measurement techniques also confirmed the reliability of LOPAP to
113 quantify HONO in the polluted regions.^{34,36,37} Other instruments for key-related species (VOCs,
114 OVOCs, NO, NO₂, NH₃, O₃, H₂O₂, CO, PM_{2.5}, particle size distribution, and composition, etc.) and
115 meteorological parameters (pressure, temperature, relative humidity (RH), J(NO₂), etc.) are
116 summarized in Table S1. The external sampling unit of LOPAP and inlets of other instruments were
117 installed about 3.4 m above the ground level. The distance between every two inlets or sampling
118 units were less than 20 m. Note that NO₂ measured by chemiluminescent technology used in this
119 campaign may overestimate ambient NO₂ by the interference from HONO, HNO₃, etc., and the
120 validation of NO₂ was therefore conducted in section 3 of the SI.

121 **Model description**

122 A 0-D box model MCM v3.3.1³⁸ was used to simulate the radical concentration and budget, the
123 HONO budget, and the potential particle nitrate formation rate, P(HNO₃), from gas-phase reaction
124 NO₂+OH. The chemical mechanistic information was taken from the MCM v3.3.1 website
125 (<http://mcm.leeds.ac.uk/MCM>) as the basic mechanism for the simulation. The model was run from
126 3rd to 24th December 2017 with a time step resolution of 1 hour and initiated by a 2-day spin-up for
127 the first day. All the photolysis frequencies, except J(NO₂) were calculated by the model and were
128 scaled by the ratio measured to modeled J(NO₂). More details about the model are shown in the SI.
129 Although atmospheric OH concentration is essential for the HONO budget analysis, unfortunately,
130 no radical measurements were available during this campaign. Therefore, we run the model with
131 constraints on all measured parameters (case name: with HONO) to simulate the OH concentrations.
132 The simulated OH concentrations and budget were comparable with other winter measurements of
133 OH (Figure S1-S3 and Section 1.2 in the SI). To reveal the contribution of atmospheric HONO to
134 OH concentration and P(HNO₃), another case with the constraints on all the measured parameters
135 but without HONO (case name: without HONO) was also conducted. Then we parameterized the
136 proposed HONO sources and added each of them in the basic mechanism separately for sensitivity
137 tests. Briefly, Table 1 summarizes the model configuration for HONO simulations, of which 10
138 model scenarios from S-0 to S-9 were set. The scenario S-0 was the base case, which only contained
139 the default HONO source NO+OH. Scenarios from S-1 to S-6 were to test the sensitivity of each
140 HONO source including direct emission, the dark NO₂ uptake on ground surfaces, the dark NO₂
141 uptake on aerosol surfaces, the photosensitized NO₂ uptake on ground surfaces, the photosensitized
142 NO₂ uptake on aerosol surfaces, and the photolysis of particle nitrate. For the photolysis frequency
143 of pNO₃, J(pNO₃), the same diurnal shape as the gas-phase photolysis of HNO₃ (J(HNO₃)) was
144 assumed³⁹. Therefore, an enhancement factor (EF = J(pNO₃) / J(HNO₃)) due to faster particle nitrate
145 photolysis than gas-phase HNO₃ was deployed in the model to characterize the photolysis of particle

146 nitrate as well as the HONO production. For the sensitivity tests, a typical parameter (emission ratio
 147 for direct emission, NO₂ uptake coefficients for heterogeneous reaction and EF for particle nitrate)
 148 and the upper/lower limit for each source were scaled by the proposed larger/smaller parameters or
 149 a variation factor (see the SI, Section 2).

150 The photosensitized heterogeneous reaction of NO₂ on ground surfaces has been proved to have a
 151 significant impact on HONO budget^{25,40-45}, especially for ground base measurements like this study
 152 with a sampling height (3.4 m) close to the ground source. However, the impact may depend on the
 153 NO₂ levels, e.g., recent laboratory studies found that the photo-enhanced uptake coefficient of NO₂
 154 on surfaces remarkably slowed down with increasing NO₂ concentration^{16,17}. Considering
 155 atmospheric NO₂ concentrations at the sampling site were usually high, i.e., averaged NO₂ was
 156 about 20±10, 29±12, and 39±14 ppbv in CP, HP and HHP, respectively, two additional scenarios S-
 157 8 and S-9 with reducing photosensitized NO₂ uptake coefficients by 30% and 60% were also tested.
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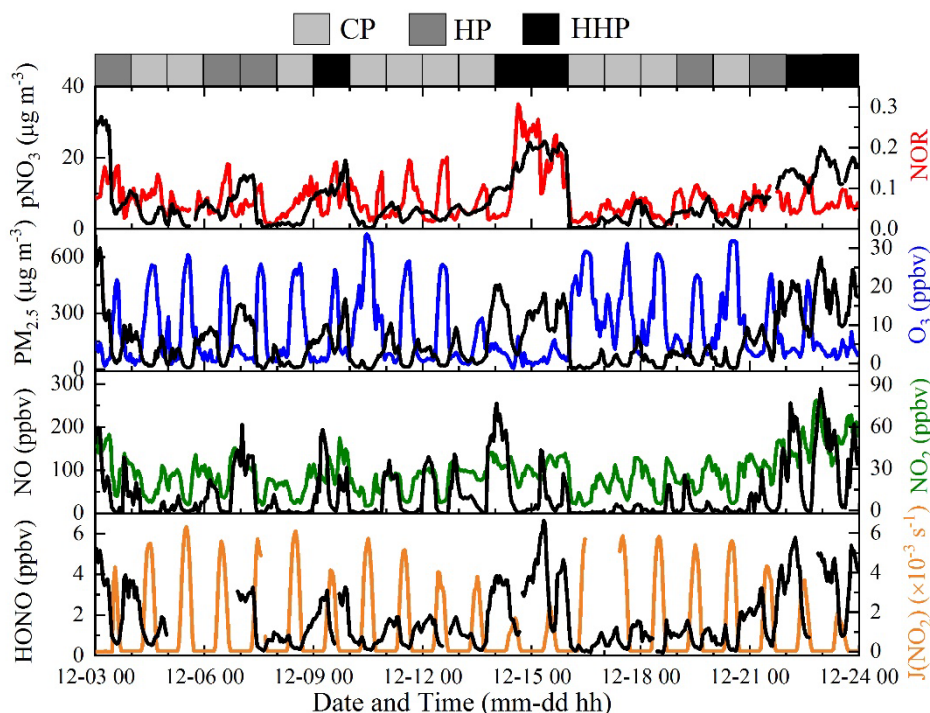
159 Table 1. Configurations of the model simulations for different HONO source scenarios. α : the
 160 emitted ratio of HONO to NO_x for direct emission; EF: enhancement factor of the photolysis
 161 frequency of particle nitrate compared to that of gas-phase HNO₃ (EF= J(pNO₃)/J(HNO₃)). From
 162 S-1 to S-6, sensitivity tests on the sources were conducted with the corresponding parameters scaled
 163 by the typically used, the lower limit, and the upper limit values (see details in the SI).

Scenarios	Configuration
S-0	NO + OH + M → HONO + M
S-1	S-0 + direct emission ($\alpha=0.8\%$, 0.3%, 1.6%) ⁹⁻¹²
S-2	S-0 + dark NO ₂ uptake on ground surfaces ($\gamma_1=1\times 10^{-6}$, 0.2×10 ⁻⁶ , 5×10 ⁻⁶) ¹⁴⁻¹⁷
S-3	S-0 + dark NO ₂ uptake on aerosol surfaces ($\gamma_1=1\times 10^{-6}$, 0.2×10 ⁻⁶ , 5×10 ⁻⁶) ¹⁴⁻¹⁷
S-4	S-0 + photosensitized NO ₂ uptake on ground surfaces ($\gamma_2=1.35\times 10^{-5}$, 0.27×10 ⁻⁵ , 6.75×10 ⁻⁵) ¹⁴⁻¹⁷
S-5	S-0 + photosensitized NO ₂ uptake on aerosol surfaces ($\gamma_2=1.35\times 10^{-5}$, 0.27×10 ⁻⁵ , 6.75×10 ⁻⁵) ¹⁴⁻¹⁷
S-6	S-0 + photolysis of particle nitrate (EF=30, 1, 100) ^{18-20,31,32}
S-7	S-0 + all the tested sources
S-8	S-7 with 0.7× γ_2
S-9	S-7 with 0.4× γ_2

164

165 **Results and Discussion**

166 **Overview of the observations**



167

168 Figure 1. Time series of HONO and related parameters measured during the campaign. The light
 169 gray, dark gray, and black areas on the top part represent the pollution levels of the clean periods
 170 (CP), haze periods (HP), and heavy haze periods (HHP), respectively. On the left axis, HONO, NO,
 171 PM_{2.5}, and pNO₃ (particle nitrate) are shown in black lines in each layer from bottom to the top.
 172 J(NO₂) (photolysis frequency of NO₂), NO₂, O₃, and NOR (nitrogen oxidation ratio)
 173 are shown in yellow, green, blue, and red lines on the right axis, respectively.

174

175 Time series of HONO, particulate matter with a diameter of less than 2.5 µm (PM_{2.5}), particle nitrate
 176 (pNO₃), NO, NO₂, O₃, photolysis frequency of NO₂ (J(NO₂)) and NOR (nitrogen oxidation ratio,

177
$$NOR = \frac{n NO_3^-}{n NO_3^- + n NO_2}$$
⁴⁶ are shown in Figure 1. The air temperature (Temp), relative humidity (RH)

178 particle surface area density (PS), and ammonia mixing ratios (NH₃) are illustrated in Figure S4. Air
 179 pollution at this rural site was severe, e.g., the hourly levels of PM_{2.5} and NO_x (NO+NO₂) frequently
 180 exceeded 100 µg m⁻³ and 100 ppbv, respectively. Campaign averaged levels of HONO, PM_{2.5}, pNO₃,
 181 NO, and NO₂ were 1.8±1.4 ppbv, 98±112 µg m⁻³, 8.0±7.0 µg m⁻³, 45±62 ppbv and 27±14 ppbv,
 182 respectively. In particular, the averaged daytime (7:00-17:00 local time) HONO mixing ratio at this
 183 site could achieve as high as 1.3±1.3 ppbv, which was remarkably higher than those observed in
 184 European or American cities⁴⁷⁻⁴⁹, but comparable to those observed in the NCP²⁹ and Santiago de
 185 Chile⁵ (Table S2). The averaged daytime HONO/NO_x ratio was 3.3%±1.7% which was much higher
 186 than those from direct emission (0.3%-1.6%)⁹⁻¹², suggesting atmospheric HONO at the rural site
 187 was dominated by the sources other than direct emissions especially after considering the much

188 longer lifetime of NO_x than HONO during the daytime. The relatively high levels of HONO at the
189 rural site were suspected to be the dominant source for atmospheric OH, and thus played an essential
190 role in the formation of secondary pollutants, e.g., evident and frequent increase of NOR and pNO₃
191 concentrations during the daytime could be identified in Figure 1.

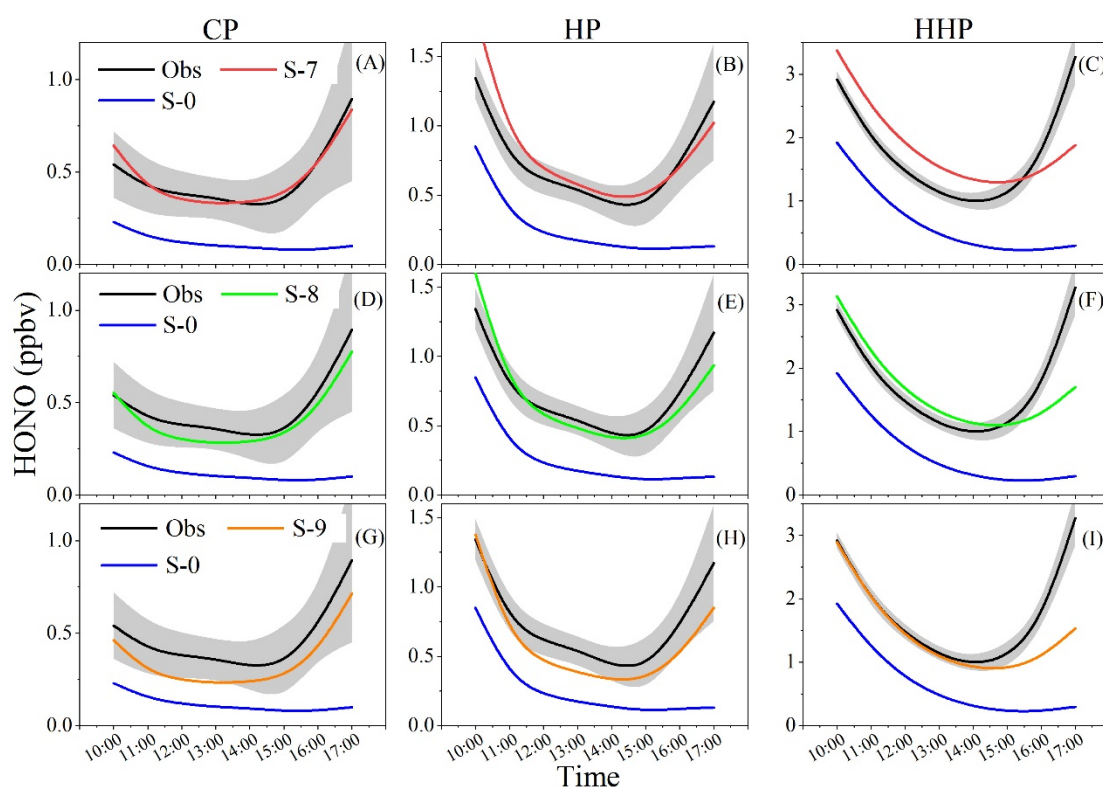
192 To better understand the daytime sources for HONO, as well as the interaction between HONO and
193 nitrate, the field data were classified into three classes: clean periods (CP, 11 days) when the
194 averaged PM_{2.5} concentrations during daytime were below 50 μg m⁻³, haze periods (HP, 5 days)
195 when PM_{2.5} concentrations were in the range of 50-150 μg m⁻³ and heavy haze periods (HPP, 5 days)
196 when PM_{2.5} concentrations were above 150 μg m⁻³. The averaged diurnal variations and
197 concentrations of HONO and related parameters during different pollution periods are shown in
198 Figure S5 and Table S3. Daytime HONO increased by a factor of 3 during the HPP to the CP, while
199 the solar intensity only decreased by a factor of 2. Therefore, the OH production rate through HONO
200 photolysis was expected to be larger in the HPP. Besides, NO₂ during the HPP also increased by a
201 factor of 3 to the CP, which would promote the reaction of NO₂ with OH, leading to the faster
202 daytime particle nitrate formation during the HHP. Furthermore, the exceptionally high mixing
203 ratios of HONO precursors, including NO_x and particle nitrate during the HHP might also accelerate
204 HONO formation through the heterogeneous reactions of NO_x or photolysis of particle nitrate,
205 resulting in a remarkable increase of HONO during HPP.

206 **HONO simulation and budget**

207 Model results from the base case (S-0) and sensitivity tests on each HONO source (S-1 to S-6) are
208 shown in Figure S6 and S7. The default HONO source, the homogeneous reaction of NO with OH
209 (S-0), was not able to explain the observations (Figure S6), suggesting additional daytime HONO
210 sources. With the presence of direct emission (S-1), the dark heterogeneous reactions of NO₂ on the
211 ground surfaces (S-2) or aerosol surfaces (S-3), the modeled daytime HONO was still much lower
212 than the observations (Figure S6). However, the model could well reproduce the observations during
213 most of the daytime (from 10:00 to 15:00) when a median value of the uptake coefficient was
214 adopted for the photosensitized heterogeneous reaction of NO₂ on ground surfaces, and the upper
215 and lower limits could well cover the observations in the three periods (Figure S7, A to C), indicating
216 the possible important role of photosensitized heterogeneous reaction of NO₂ on ground surfaces in
217 daytime HONO formation. In contrast, both the photo-enhanced sources of the photosensitized
218 heterogeneous reaction of NO₂ on aerosol surfaces and the photolysis of particle nitrate showed a
219 negligible impact on daytime HONO formation even when the uptake coefficient or EF were
220 enlarged (Figure S7, D to I). The large difference for the sensitivities between the photosensitized
221 heterogeneous reactions of NO₂ on ground surfaces and particle surfaces was mainly ascribed to the
222 much larger S/V ratio of ground surfaces than that of particle surfaces (e.g., an average of 1.2×10^{-3}
223 m⁻¹ in this study)^{44,50,51} with the similar NO₂ uptake kinetics on particle and ground surfaces.

224 Figure 2 shows the model results of scenarios from S-7 to S-9 with inputting all the additional
225 sources. With the typical photosensitized NO₂ uptake coefficient on the ground surfaces (S-7), the
226 model could well reproduce the observed daytime HONO (0.9% overestimation) during the CP
227 (Figure 2A), but distinctly overestimated HONO during the HP and HHP (Figure 2B and C). In the
228 scenario S-8, the photosensitized NO₂ uptake coefficient was reduced by 30%, for which modeled
229 HONO was much closer to the observation (3.6% underestimation) during the HP (Figure 2E) but

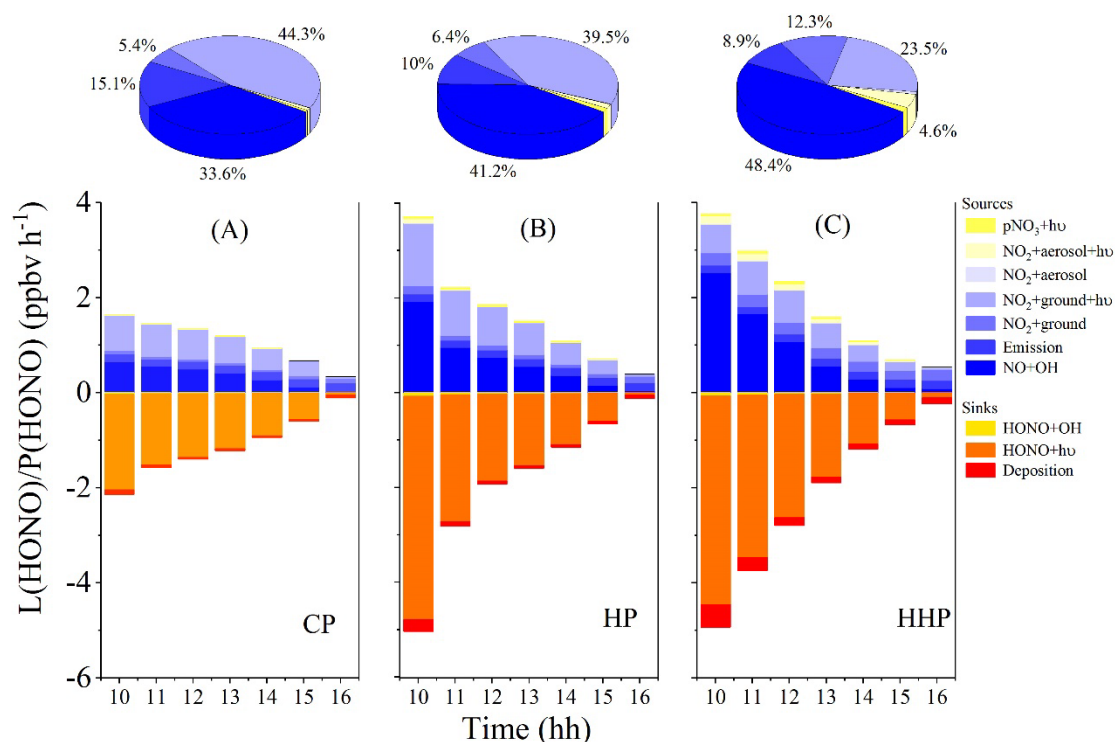
230 still higher than the observations during the HHP (Figure 2F). The observed HONO during the HHP
 231 could be partially reproduced when the photosensitized NO₂ uptake coefficient was reduced by
 232 another 30% in S-9 (Figure 2I). The modeled HONO in S-9 could well explain the observation in
 233 the morning and noontime (10:00-15:00, 1.7% underestimation) but still underestimated HONO in
 234 the late afternoon (32.5% underestimation), which was perhaps caused by an overestimation of
 235 MLH or the relative small dark NO₂ uptake coefficient on the ground surfaces, leading to the
 236 underestimation of ground HONO formation. With a larger dark NO₂ uptake coefficient on the
 237 ground surfaces during the sensitivity tests, the model could well reproduce the observed HONO
 238 (Figure S6F), which may act as evidence that the dark NO₂ uptake on the ground surfaces was
 239 underestimated in the afternoon of HHP.
 240



241
 242 Figure 2. Model results of diurnal profiles of simulated and observed daytime HONO during
 243 different periods (CP: clean periods, HP: haze periods, HHP: heavy haze periods). Throughout the
 244 whole graph, the black lines represent the observed average diurnal HONO variation with the
 245 standard deviation as the shaded area. The blue lines represent the model HONO mixing ratios in
 246 the base case S-0. The red, green and orange lines represent the model HONO results in the case S-
 247 7, S-8 and S-9, respectively. Similar to the observation, all the model results were classified into
 248 three periods to assess the model performance during different pollution periods.
 249

250 With gradually reducing the photosensitized NO₂ uptake coefficients, model performance on HONO
 251 simulations for the polluted periods (HP and HHP) was largely improved, which suggests that the
 252 NO₂ uptake coefficients depended on the pollution levels of NO₂ as observed in laboratory
 253 studies^{16,17}. Although in some model studies the uptake coefficients were already scaled by RH and
 254 light intensity^{50,52} leading to a significant improvement to explore the HONO budget and the SOA
 255 formation^{33,52}, etc., the still existing differences between observations and simulations are possibly

256 caused by the missing parameterization of the NO₂ uptake kinetics by the pollution levels as
 257 discussed in the present study for the first time. The observed HONO in different pollution periods
 258 was well reproduced by the model, implying that more similar analysis is still necessary to better
 259 understand HONO formation by the models in the polluted areas like the NCP.
 260



261
 262 Figure 3. Diurnal HONO budget and the relative contribution from each source during different
 263 periods (CP: clean periods, HP: haze periods, HHP: heavy haze periods). The histograms and the
 264 pie charts contain the HONO source (positive) and sink (negative) strengths, and the corresponding
 265 relative contributions from each HONO source. The pie charts show the averaged relative
 266 contribution of each HONO source to HONO formation (10:00-17:00) during CP, HP, and HHP,
 267 respectively. Only the contribution larger than 2% is marked in the pie charts.
 268

269 The diurnal HONO budget and the relative contribution from each source during each period are
 270 shown in Figure 3. Apparently, the total HONO sink strength was slightly larger than the total source
 271 strength in the daytime, which was consistent with the daytime decreasing trend of the observed
 272 HONO. Among the six HONO sources, the homogeneous HONO formation from the gas phase
 273 reaction of NO+OH always acted as one of the essential sources for HONO, accounting for 33.6%,
 274 41.2% and 48.4% of daytime HONO formation during the CP, HP, and HHP, respectively. The
 275 significant increase of the contribution for the gas phase reaction to atmospheric HONO from the
 276 CP to the HHP was mainly ascribed to the remarkable increase of daytime NO, e.g., the NO
 277 concentration increased by a factor of ca. 7 from the CP to the HHP (Table S3) while the OH
 278 concentration only declined by a factor of less than 3 (Figure 5). Additionally, the reaction of
 279 NO+OH made a more significant contribution to HONO at noontime during the CP and in the early
 280 morning during the HP and HHP (Figure S8), which could be explained by the relatively high OH
 281 concentrations at noontime during the CP (Figure 5) and the relatively high NO in the early morning
 282 during the HP and HHP (Figure S5). The significant contribution from the homogeneous formation

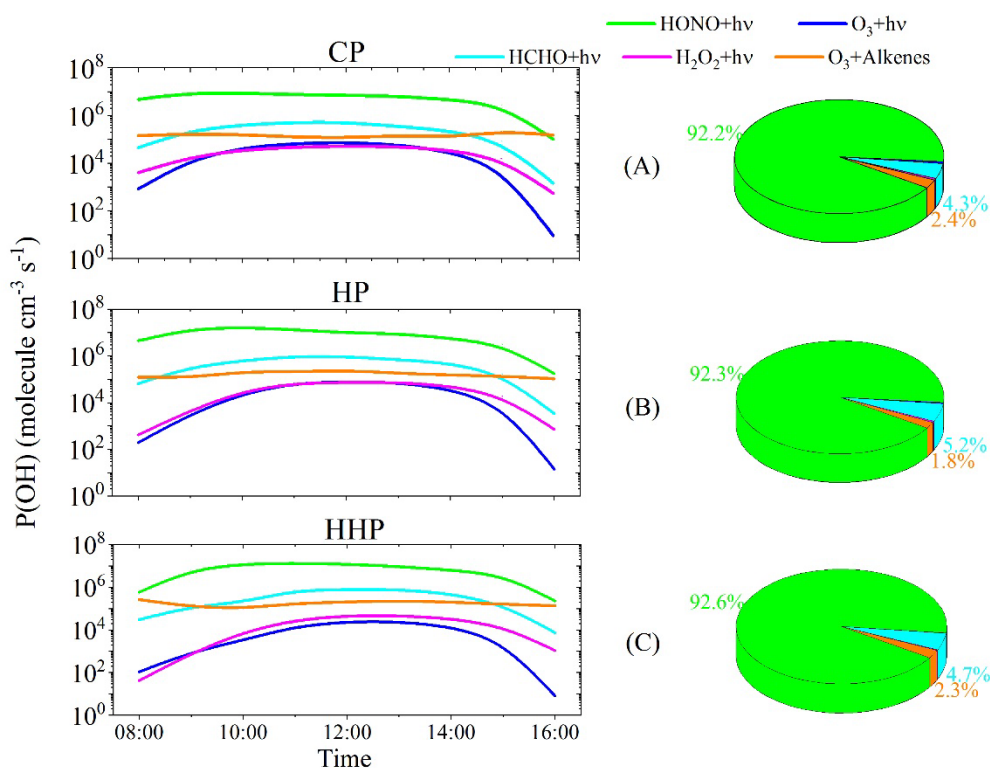
283 of HONO was also found at other high-NO_x sites such as London⁴⁷, Beijing^{8,53}, Tai Wan⁵⁴, and
284 Santiago de Chile⁵⁵. Nevertheless, the formation of HONO by this gas-phase reaction does not
285 represent a net OH source, since the same quantity of OH radicals is consumed compared to the OH
286 formation by the subsequent HONO photolysis. Thus, for the future, additional measurements of
287 OH radical concentrations are recommended to better quantify net OH initiation by HONO
288 photolysis. In contrast to the gas phase reaction of NO+OH, the contribution of the photosensitized
289 heterogeneous reactions of NO₂ on ground surfaces to atmospheric HONO exhibited a declining
290 trend from the CP to the HPP, with the contributions of 44.3%, 39.5% and 23% during the CP, HP,
291 and HPP, respectively. The contribution of the dark heterogeneous reaction of NO₂ on the ground
292 surfaces to atmospheric HONO increased with increasing NO₂ concentrations from the CP to the
293 HHP, with a contribution of 5.4% in the CP, 6.4% in the HP and 12.3% in the HHP. The proportion
294 of the direct HONO emission to the total daytime HONO formation gradually decreased from 15.1%
295 in the CP to 10% in the HP and 8.9% in the HHP, which was mainly ascribed to the significant
296 increase of HONO source from the gas phase reaction of NO with OH. Both the dark heterogeneous
297 reaction and the photosensitized heterogeneous reaction of NO₂ on aerosol surfaces made small
298 contributions to HONO formation, with the largest contribution of about 4.6% during HHP when
299 both aerosol and NO₂ concentrations were very high, which is in agreement with previous
300 studies^{50,56}. Although the photolysis of pNO₃ has been proposed as one important source for
301 atmospheric HONO, the contribution from pNO₃ photolysis to HONO formation was found to be
302 negligible (<2%) even during the HHP with high pNO₃ concentrations. As discussed before, the
303 photolysis of pNO₃ was not sensitive to EF values in the range of 1 to 100 and the modeled HONO
304 in S-6 was much lower than the observation (Figure S7), suggesting that the photolysis of pNO₃ is
305 not expected to play an important role in the HONO budget during wintertime at high-NO_x polluted
306 regions such as the rural NCP in this study.

307 The HONO loss through photolysis was the major sink, accounting for more than 90% of the HONO
308 loss during the daytime. The reaction of HONO + OH contributed ca. 3.5% to the HONO loss during
309 the CP, 1.5% during the HP and 1.4% during the HHP because of the relatively higher OH during
310 the CP than the HP and HHP (Figure 5). In contrast, the deposition contributed to more significant
311 loss of HONO during the HHP (9%) than the CP (3%) and the HP (5%) because of the relatively
312 higher HONO concentrations during HHP than CP and HP (Figure S5).

313 Based on HONO budget results, the photosensitized heterogeneous reaction of NO₂ on ground
314 surfaces played an important role in the HONO budget, suggesting a vertical distribution of HONO.
315 A rough estimation of the vertical distribution (Figure S9) calculated based on atmospheric
316 turbulence (see details in SI) indicates that in the upper boundary layer, the role of HONO was
317 expected to be less important than that at ground level, but may still significant, especially in
318 polluted periods. Gradient HONO measurements should be conducted in the NCP to better quantify
319 the impact of HONO on HO_x chemistry in the atmospheric boundary layer⁵⁷ and regional air
320 pollution such as O₃, SOA, and nitrate pollution. The aerosol-derived HONO sources, including
321 heterogeneous reactions on aerosol surfaces and the photolysis of pNO₃, did not make a significant
322 contribution to HONO formation. High EFs could increase the HONO formation from pNO₃
323 photolysis but should be carefully considered in model studies. More detailed, perhaps in-situ
324 research at ambient conditions³², especially in the high NO_x and high nitrate polluted areas, e.g., the
325 NCP and other similar regions, are recommended.

326 Implications on HO_x chemistry and nitrate formation

327 To explore the role of HONO in radical formation, we summarized the net primary OH production
 328 from five sources in the model, i.e., HONO photolysis (subtracted by the OH loss through NO +
 329 OH and HONO + OH), O₃ photolysis, HCHO photolysis (HCHO→H/HCO→HO₂→OH, here only
 330 primary emitted HCHO (37%) was considered), H₂O₂ photolysis, and ozonolysis of alkenes. The
 331 diurnal net OH production rate, P(OH), from each source, and its corresponding contribution to the
 332 total daytime OH production during each pollution period are shown in Figure 4. It is apparent that
 333 the net OH production from HONO photolysis, P(OH)_{HONO, net}, was always more than one order of
 334 magnitude larger than those from the other four sources, especially in the morning when P(OH)_{HONO, net},
 335 was 2-3 orders of magnitude larger than others, dominating the total OH initiation. As a result,
 336 P(OH)_{HONO, net} maintained at a high level (between 10⁶-10⁷ molecules cm⁻³ s⁻¹) and played the most
 337 important role in OH formation throughout the daytime. Compared to the CP, the solar radiation
 338 during the HHP decreased by a factor of 2 (Figure S5E). However, P(OH)_{HONO, net} during the HHP
 339 was comparable to or even larger than that during the CP (Figure 4), which was because of the
 340 increase of HONO by a factor of about 3 (Figure S5A). The mean daytime primary OH production
 341 rates were 5.6×10⁶, 8.0×10⁶ and 7.0×10⁶ molecules cm⁻³ s⁻¹ during CP, HP, and HHP, respectively,
 342 which were comparable to winter measurements in Weld Country⁴, Santiago de Chile⁵, and
 343 suburban Beijing⁶, and also to some summer measurements at this place⁷, etc. The daytime OH
 344 radical concentrations (Figure S1), however, were much lower than those in summer measurements,
 345 suggesting much higher OH reactivity (k_{OH})⁴⁻⁸ from the elevated levels of atmospheric pollutants
 346 including NO_x (Figure 1 and Figure S4) and VOCs, leading to enhanced formation of secondary
 347 pollutants (e.g., nitrate and SOA, etc.).
 348



349

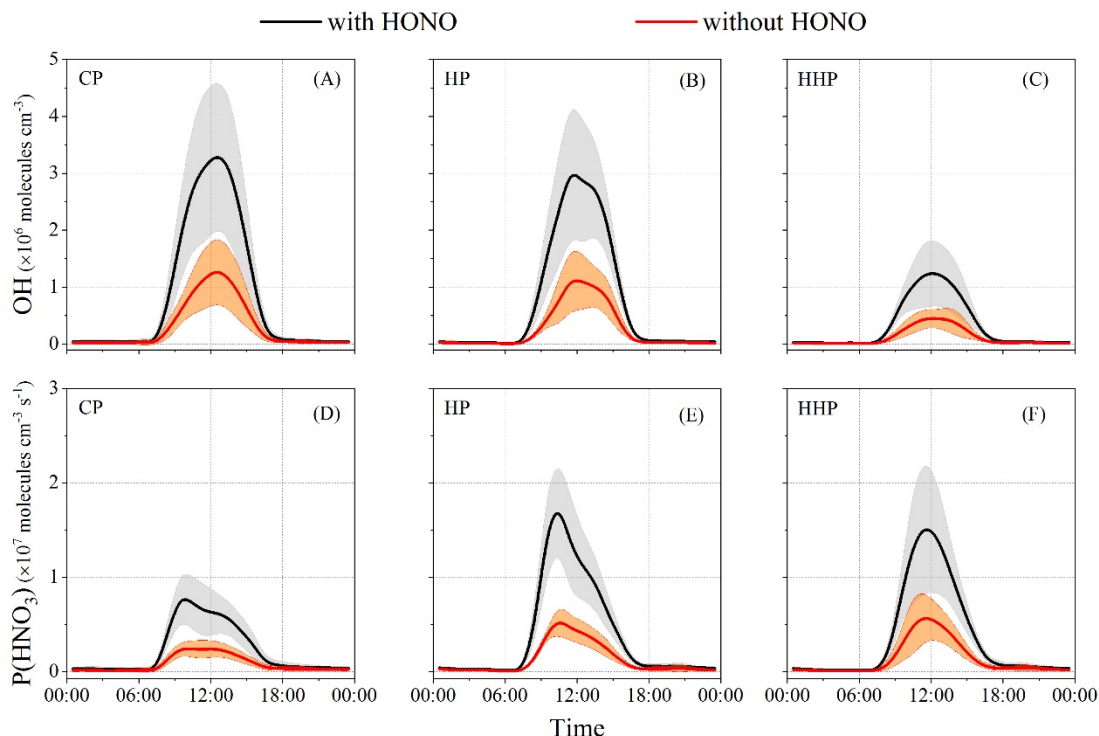
350 Figure 4. Modeled net OH production rates from five sources and their corresponding relative

351 contribution. The colors of green, blue, cyan-blue, pink and orange represent the net primary OH
 352 production from HONO photolysis, O₃ photolysis, HCHO photolysis, H₂O₂ photolysis and the
 353 ozonolysis of alkenes (O₃+Alkenes), respectively. Both the contribution of O₃ photolysis and H₂O₂
 354 photolysis is less than 2% during the three periods. Note that net primary OH production from
 355 HONO was the production of OH through HONO photolysis subtracted by the OH loss through
 356 NO+OH and HONO+OH. Only direct emitted HCHO could produce net primary OH
 357 (HCHO→H/HCO→HO₂→OH) and the contribution of direct HCHO emission to the observation
 358 was 37% during the campaign estimated by multiple linear regression between HCHO, CO
 359 (indicator for direct emission) and O₃ (indicator for secondary formation).

360

361 Throughout the whole campaign, the contribution to the total primary OH production from HONO
 362 photolysis was about 92% (Figure 4). To the best of our knowledge, the largest contribution of
 363 HONO to OH reported by previous non-polar⁵⁸ studies was 80.4% with P(OH)_{HONO, net} of 3.1×10⁶
 364 molecules cm⁻³ s⁻¹ in Weld Country, Colorado⁴, both of which are, however, much lower than those
 365 in this study, suggesting a higher oxidizing capacity and more active photochemistry in the winter
 366 at this site. The second-largest primary OH source was the photolysis of HCHO and its contribution
 367 was always between 4%-5%, which was because of the adverse trends of HCHO concentrations
 368 (low values during CP and high values during HHP) and photolysis frequency (high values during
 369 CP and low values during HHP) during the three periods. Compared to HONO photolysis, the
 370 ozonolysis of alkenes, O₃ photolysis or H₂O₂ photolysis made a negligible contribution (less than
 371 2%) to OH production due to their low concentrations or low photolysis frequencies.

372



373

374 Figure 5. Diurnal profiles of OH concentrations and potential total nitrate formation rate from gas-
 375 phase reaction NO₂+OH (P(HNO₃)) with or without constraint on HONO. The shaded areas
 376 represent the standard deviation.

377

378 High OH production rates due to fast HONO photolysis lead to high oxidizing capacity with
379 maximum averaged OH concentrations of 3.3×10^6 , 3.1×10^6 and 1.3×10^6 molecules cm^{-3} at noontime
380 during CP, HP, and HHP, respectively. High OH levels would accelerate the homogeneous formation
381 of nitrate precursor HNO_3 through the reaction $\text{NO}_2 + \text{OH}$, resulting in potential daytime integrated
382 gross nitrate production of 1.7, 3.1 and $2.9 \mu\text{g m}^{-3} \text{h}^{-1}$ in the three periods, respectively. Note that
383 the potential daytime gross nitrate production was the upper limit of the particle nitrate production
384 through this path because not all the $\text{HNO}_3(\text{g})$ transformed into particle nitrate. Then we estimated
385 the HNO_3 partitioning ratio ($\text{HPR} = \text{pNO}_3 / (\text{pNO}_3 + \text{HNO}_3)$)⁵⁹ using the measured nitrate and average
386 HNO_3 concentration from a winter measurement⁶⁰ (Figure S10). High daytime HPR was found
387 during the campaign, and HPR was higher during HHP (>0.95) than the CP (>0.8), in agreement
388 with the variation of NOR (Figure S11). Meanwhile, one study used the ISORRPIA II model also
389 found a high HNO_3 partitioning ratio in the NCP with an average of 0.8⁵⁹. In our study, NH_3
390 concentration was higher and the temperature was much lower than in Wang et al.⁵⁹ (Figure S4),
391 and therefore, the HNO_3 partitioning ratio was expected to be higher than 0.8^{30,59}. Even scaled by
392 0.8, $\text{P}(\text{HNO}_3)$ is still comparable to or even more than that in the summertime at this site (ca. $2.5 \mu\text{g}$
393 $\text{m}^{-3} \text{h}^{-1}$)⁷, suggesting the significant nitrate formation from the unexpectedly active photochemistry
394 in winter of this site. Additionally, nitrate production was able to explain the observed particle nitrate
395 concentrations of 2.1, 7.3 and $15.3 \mu\text{g m}^{-3}$ during the three periods (Table S3), which provides
396 further insight on nitrate pollution in this region. Here we did not consider N_2O_5 formed by
397 $\text{NO}_3 + \text{NO}_2$ because the modeled N_2O_5 concentrations and production rate were always 1-2 orders of
398 magnitude lower than those by the reaction of $\text{NO}_2 + \text{OH}$ in the model.

399 The dominant contribution of HONO to the OH production gave HONO an indispensable role in
400 the atmospheric oxidizing capacity and hence the secondary pollution such as nitrate (Figure 4 and
401 Figure 5) during wintertime in the NCP. Without constraints by the measured HONO, the OH and
402 HO_2 concentrations will be underestimated by a factor of at least 2, which could further result in a
403 huge underestimation of potential total nitrate formation rates by a factor of more than 2 (Figure 5
404 and S12) and the formation rates of other secondary pollution, e.g., O_3 and SOA, reinforcing the
405 important role of HONO in regional photochemistry and hence the formation of the regional air
406 pollution. Considering the increasing particle nitrate pollution (Figure S13) and the high HONO
407 levels (Figure 1) at this site and other places in the NCP³⁰ during wintertime, our study highlights
408 the critical role of HONO in the radical budget and nitrate formation. It helps to understand the
409 formation of HONO at different pollution levels in the NCP and other similar regions as well.

410 **Associated contents**

411 **Supporting Information**

412 The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.
413 Additional details about the campaign and the model, 13 figures (Figure S1-S13), and 3 tables (Table
414 S1-S3) are included.

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418 **Notes**

419 The authors declare no competing financial interest.

420 **Author contributions**

421 Y.M. designed HONO research. Y.M., J.C., and T.W. organized the field campaign. C.X. performed
422 the HONO measurement, data analysis, and model simulations. C.Z., P.L., and X.Z. performed the
423 measurement of NO, NO₂, and SO₂. C.Y. performed the measurement of H₂O₂. C.Z. and J.W.
424 performed the OVOCs measurement. H.C. and F.Z. performed the measurement of NH₃, PAN,
425 VOCs, and PM_{2.5} compositions. J.Z. and J.A. analyzed the NO_x emission flux and performed the
426 WRF-Chem simulations. J.K., Y.R., and G.K. made helpful comments and suggestions during the
427 model simulations. C.X. and Y.M. wrote this manuscript with all the authors' contributions. J.K.,
428 C.V., Y.R., and A.M. revised this manuscript.

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