High crop yield losses induced by potential HONO sources — a case study in the North China Plain

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High crop yield losses induced by potential HONO sources — a case study in the North China Plain

Nitrous acid (HONO) is a major source of hydroxyl radicals in the troposphere through its photolysis, and can significantly influence ozone (O₃) levels, thereby causing considerable crop yield losses. Previous studies have assessed relative crop yield losses by using exposure-response equations with observed or simulated O₃, however, the contribution of enhanced O₃ due to potential HONO sources to the crop yield losses has never been quantified. In this study, for the first time, we evaluated the crop yield losses caused by potential HONO sources in the North China Plain (NCP), which is one of the major grain-producing areas in China suffering from heavy O₃ pollution, by using the Weather Research and Forecasting/Chemistry (WRF-Chem) model during the wheat and maize growing seasons of 2016. HONO simulations were significantly improved after including six potential HONO sources. The potential HONO sources produced a daily maximum 8-h O₃ enhancement of 8.1/8.2 ppb during the wheat/maize growing seasons, respectively, and led to ~11.4%/3.3% relative yield losses for wheat/maize, respectively, corresponding to approximately US\$3.78/0.66 billion losses, respectively, in NCP in 2016. Potential HONO sources play a significant role in O₃ formation and may induce high crop yield losses globally.

21 Nitrous acid (HONO) is an important source of hydroxyl radicals (OH) in the troposphere, and
 22 contributes 20–80% of the primary OH production ¹⁻³ (**Table S1**) through its photolysis (R1) during
 23 the daytime:

25 However, the sources of HONO are hitherto not well understood, and the current air quality
 26 models always severely underestimate ground HONO observations by using a default chemical
 27 mechanism ⁴⁻⁸, which only considers the dominant gas-phase production of HONO, i.e., the reverse
 28 reaction of R1. To improve HONO simulations, some potential HONO sources (e.g., traffic emissions,
 29 soil emissions, inorganic nitrate photolysis, and NO₂ heterogeneous reactions on ground/aerosol
 30 surfaces) have been coupled into several air quality models ⁴⁻⁹. These HONO improvements produce
 31 more OH, which is favorable for ozone (O₃) formation in areas with high emissions of nitrogen oxides
 32 (NO_x) and volatile organic compounds (VOCs) (R2–R8).

40 O₃ in the atmosphere can affect plants mainly through stomatal-induced biochemical reactions,
41 producing reactive oxygen species, which could react with plant cell structure, and cause damage at
42 molecular, biochemical and physiological levels, and eventually lead to a decline in plant productivity
43 ¹⁰⁻¹². Atmospheric modelling studies in recent years have evaluated the impact of some potential
44 HONO sources on O₃ formation, and have shown that hourly O₃ enhancements due to the considered
45 potential HONO sources ranging from several to tens of ppb worldwide ⁴⁻⁹ (**Table. S2**). The enhanced
46 O₃ caused by the considered potential HONO sources may further damage plants and reduce the crop
47 yield, however, has not been quantified by current studies.

48 To understand the relationship between O₃ exposure and crop yield losses, some open-top chamber
49 experiments and ozone-free air-controlled enrichment experiments have been conducted globally over
50 the past decades ^{13,14}. Based on these field experiments, a series of cumulative metrics and exposure-
51 response (ER) equations have been proposed ¹³⁻¹⁸ and widely applied to evaluate the yield losses
52 worldwide. For instance, Avnery et al. ¹⁹ estimated the reduction in the global wheat and maize harvest
53 induced by O₃ and found that the relative yield losses in 2030 could reach 6.9–36% and 6.5–11.9%,
54 respectively, compared with the yields in 2000. Feng et al. ²⁰ found an increasing trend of maize yield
55 losses in the North China Plain (NCP) from 8.2% (2014) to 13.4% (2017). Zhao et al. ²¹ estimated the
56 effects of surface O₃ on crops across China during 2015–2018 and found increasing trends in wheat
57 and maize yield reductions. The national yield reduction rate of winter wheat increased from 20.1%
58 (2015) to 33.3% (2018), much larger than that of maize (from 5.0% (2015) to 6.3% (2018)), and the
59 largest losses of both crops occurred in NCP ²¹.

60 NCP is one of the major crop-producing areas in China, producing ~70% of the total wheat yield
61 and ~25% of the total maize yield in China in 2016 (**Table S3**). However, this region has high

anthropogenic emissions of NO_x and VOCs and has suffered from elevated mixing ratios of O₃^{22,23}, which would further reduce the crop yields in the future. To our knowledge, the current studies evaluated total crop yield losses by using observed or simulated O₃ mixing ratios and the ER equations, however, the effect of potential HONO sources on crop yield losses has never been assessed despite the important role of HONO in O₃ formation. In this study, we made the first attempt to quantify the crop yield losses caused by potential HONO sources for the wheat-maize rotation system in NCP in 2016 by using the updated Weather Research and Forecasting/Chemistry (WRF-Chem) model.

Results

Comparison between simulated and observed HONO/O₃

The hourly-averaged observed HONO at the rural/urban sites was 0.43/0.63 ppb, and was significantly underestimated by the model base case (0.01/0.02 ppb). However, model performance was significantly improved after inserting the six potential HONO sources (case 6S) (**Fig. 1a&b**) and the modeled average HONO was 0.60/0.55 ppb at the rural/urban sites. The values of NMB, RMSE and IOA were also significantly improved (**Table S4**) in case 6S compared with the base case. For the mean diurnal patterns of HONO at the two sites (**Fig. 1c&d**), the base case always severely underestimated the observations, and the largest values of HONO occurred around noontime due to high mixing ratios of OH favoring the homogeneous formation of HONO (NO+OH→HONO) (**Fig. 1c&d**) but were merely tens of ppt (**Table S5**). After considering the six potential HONO sources, the diurnal patterns of HONO for case 6S were significantly improved for both periods, HONO accumulated during nighttime and was photolyzed in daytime, being consistent with the observations (**Fig. 1c&d**). The relative contribution of each potential HONO source to the surface HONO mixing

ratio is shown in **Fig. S1**. The NO₂ heterogeneous reaction on the ground surface dominated nighttime and daytime HONO formation. Additionally, nitrate photolysis contributed ~5–20% of the daytime HONO; soil emissions could be neglected at 69 NCP sites during the daytime and in urban Beijing during the whole day, but could contribute ~20–30% at the rural site during nighttime; traffic emissions were small during daytime and contributed ~10% in nighttime; indoor emissions were close to the traffic emissions at the urban site (10–15%) but could be neglected in the rural areas (<1%); and the NO₂ heterogeneous reaction on aerosol surfaces was minor during daytime and contributed ~5% during nighttime. The daytime underestimation (~0.1–0.2 ppb) of HONO for case 6S may represent unknown sources of HONO.

The 69-site-averaged hourly O₃ simulations were significantly improved for the 6S case compared with the base case overall (**Fig. S2**). The averaged O₃ diurnal variations during the wheat and maize growing seasons are presented in **Fig. 1e&f** and **Table S6**. Clearly, the potential HONO sources significantly enhanced daytime O₃ and narrowed the model underestimation (**Fig. 1e&f**) due to more OH and HO₂ production caused by the improved HONO (**Fig. S3&S4**). The daily maximum 8-h (10:00–17:59) (DMA8) O₃ was 45.9 (base case), 53.8 (6S case) and 57.4 (Obs) ppb during the wheat growing season (**Table S6**), whereas it was 56.7 (base case), 65.6 (6S case) and 64.5 (Obs) ppb during the maize growing season (**Table S6**). During the two growing seasons (**Fig. S5**), we found a significant enhancement in the net O₃ production rate in case 6S after considering the six potential HONO sources (**Fig. S5**), and the enhanced O₃ caused by the potential HONO sources could further damage plants and cause crop yields reduction.

Fig. 1 | Comparison of simulated (Base and 6S cases) and observed hourly and diurnal HONO mixing ratios at the rural (a&c) and urban (b&d) sites in summer of 2016, and comparison of simulated (Base and 6S cases) and observed 69-site-averaged diurnal O₃ in the North China Plain during the wheat (e) and maize (f) growing seasons in 2016.

O₃ distributions and enhancements due to improved HONO

The spatial patterns and enhancements of O₃ in NCP are shown in **Fig. 2**. During the wheat growing season, the DMA8 O₃ for the base case was 40–55 ppb in most areas of NCP (**Fig. 2(a1)**), while that for the 6S case was 50–65 ppb, decreasing gradually from south to north (**Fig. 2(b1)**), and the corresponding enhancement (**Fig. 2(c1)**) also showed a descending trend from south (~10–12 ppb) to north (~5 ppb). The regional-averaged DMA8 O₃ enhancement was 8.1 ppb (exclusive of O₃ over the ocean) (**Fig. S6**), in case 6S compared to the base case. During the maize growing season, the simulated DMA8 O₃ mean was ~40–65 ppb for the base case (**Fig. 2(a2)**) and ~50–75 ppb for the 6S case (**Fig. 2(b2)**) from July to September, being larger than that in spring due to higher temperature and stronger solar radiation. The spatial patterns showed a decreasing trend from west to the east for both cases,

118 and the enhancement also gradually decreased from west (~12–15 ppb) to the east (~5–8 ppb) (**Fig.**
 119 **2(c2))** with a mean value of 8.2 ppb excluding the ocean (**Fig. S6**). Considering the positive
 120 relationship between O₃ mixing ratios and crop RYLs, a higher RYL induced by the potential HONO
 121 sources would probably occur in southern NCP for wheat, and in western NCP for maize.

122

123

124 **Fig. 2** | Daily maximum 8-h (10:00–17:59) surface O₃ simulations for the base (a1/a2) and 6S cases (b1/b2) and
 125 the enhancements (c1/c2) induced by the potential HONO sources during the wheat/maize growing season.

126

127 RYL caused by the potential HONO sources in NCP

128 Based on the hourly simulated O₃, the 14 ER equations (**Table 1**) for the base and 6S cases were used,
 129 the corresponding RYLs caused by the potential HONO sources were calculated in NCP and are shown

130 in **Fig. 3** and **Table S7**. For wheat, large RYL variations can be found between those equations. The
 131 largest RYL mean was 0.207 as calculated by equation SUM06_1, whereas the smallest RYL mean
 132 was 0.030 as calculated by equation M7_1; the RYL mean calculated by the nine equations was 0.114,
 133 while the median mean was 0.108. For maize, the overall RYL was much smaller than that for wheat
 134 because of its higher resistance to O₃ exposure; the largest RYL mean was 0.058 (AOT40_6), and the
 135 smallest RYL mean was 0.012 (M7_2); the RYL mean calculated by the five equations was 0.033,
 136 while the median mean was 0.032. Considering the large variations of RYL among different equations
 137 and the complex crop response to O₃ exposure among diverse cultivars²⁴, the mean RYL value for
 138 wheat (0.114) and maize (0.033) could be more representative than that of a single equation, thus, we
 139 can derive that HONO induced ~11.4% and ~3.3% of RYL for wheat and maize, respectively, in NCP
 140 in 2016.

141
 142 **Fig. 3** | Box plots of the relative yield loss (RYL) induced by the potential HONO sources calculated by the 14
 143 exposure-response (ER) equations in NCP in 2016.

144 The spatial patterns computed by the nine RY equations for wheat are shown in **Fig. S7**. The RY
 145 for the base case decreased from north to south for all the equations; after considering the potential

146 HONO sources, a noticeable reduction of RY can be seen in southern NCP (**Fig.S7**). The spatial
 147 variation of RYL also showed that higher losses occurred in southern NCP, and relatively lower losses
 148 occurred in northern NCP (**Fig. S7**), corresponding to the DMA8 O₃ spatial patterns and enhancements
 149 during the growing season (**Fig. 2(a1-c1)**). The spatial patterns computed by the five RY equations for
 150 maize are given in **Fig. S8**. Maize was relatively insensitive to O₃ exposure compared with wheat.
 151 Smaller RY values occurred in western NCP for both cases (**Fig. S8**) with higher DMA8 O₃ (**Fig. 2(a2-**
 152 **b2)**), and larger RYL values also occurred in western NCP (**Fig. S8**) with higher O₃ enhancements (**Fig.**
 153 **2(c2)**).

154 For the 69 O₃ observational sites, the mean RYL values of the base (RYL_{base}) and 6S (RYL_{6S}) cases
 155 and observed O₃ (RYL_{Obs}) were calculated (E8–E10) for each of the fourteen ER equations (**Fig.**
 156 **4a&b**). Among these results, RYL_{base} showed the smallest value due to the lowest O₃ mixing ratio,
 157 RYL_{6S} was in the middle and the difference between RYL_{6S} and RYL_{base} represented the RYL caused
 158 by the enhanced O₃ induced by the potential HONO sources, while RYL_{Obs} showed the largest value
 159 and represented the actual RYL calculated by using the observed O₃, which is comparable with the
 160 RYL reported by Feng et al. ²⁰ and Zhao et al. ²¹ in the same region in 2016. The calculated relative
 161 contribution is shown in the lower panel of **Fig. 4**. Although the RYL showed a large variation when
 162 using different equations (**Fig. 4a&b**), the relative contribution for each of the equations used remained
 163 relatively stable (**Fig. 4c&d**), especially for wheat, ranging from 27.32% (AOT40_4) to 42.71%
 164 (W126_2), with a mean of 32.67% (**Fig. 4c**). The relative contribution for maize ranged from 34.34%
 165 (M12) to 75.33% (W126_3), with a mean of 39.56% (excluding W126_3 with small RYL values and
 166 large standard deviation (SD)) (**Fig. 4d**). From the above analysis, we can conclude that the enhanced
 167 O₃ caused by the potential HONO sources contributed ~30% of the actual RYL for wheat, and ~40%

168 of the actual RYL for maize in NCP in 2016.

169

170 **Fig. 4** | The 69-site-averaged relative yield loss (RYL) values calculated by using 14 Exposure-Response (ER)
 171 equations for the base (RYL_{base}, light blue histogram) and 6S (RYL_{6S}, light red histogram) cases and observed
 172 O₃ (RYL_{obs}, gray histogram) for wheat (a) and maize (b); and the relative contribution of the RYL caused by the
 173 enhanced O₃ (O₃ simulations of the 6S case minus those of the base case) to the actual RYL (RYL_{obs}) for wheat
 174 (c) and maize (d).

175

176 **Uncertainties analysis.**

177 The uncertainties of γ and f in the surface HONO simulations were assessed and the corresponding
 178 results are given in **Fig. S9**. The values of γ and f were 2.00×10^{-5} , 2.75×10^{-5} , and 5.00×10^{-5} and 0.40,
 179 0.55, and 1.00 for $\alpha = 300$, 200, and 100, respectively, when the noontime SR reached 900 W m^{-2} .
 180 Changes in α values led to slight variations in the HONO simulations but did not change the dominant
 181 daytime HONO pattern.

The impact of the four $J_{\text{nitrate}}/J_{\text{HNO}_3}$ ratios on the surface HONO simulations is shown in **Fig. S10**.

A $J_{\text{nitrate}}/J_{\text{HNO}_3}$ ratio of 1 showed a minor HONO increment of only 1–5 ppt, and a ratio of 7 merely increased HONO by ~10–20 ppt after sunrise and could be neglected after noontime; when the ratio increased to 30, HONO enhancements reached ~20–40 ppt after sunrise and ~10–20 ppt in the afternoon; and a ratio of 120 led to a HONO enhancement of ~0.1 ppb after sunrise and ~0.05 ppb in the afternoon. The true value of nitrate photolysis frequency in the atmosphere is still open to debate²⁵⁻²⁷, and we chose a conservative value of 30 for the 6S case simulation in this study. Besides, we used a relatively low soil HONO emissions in this study. As reported by Xue et al.²⁸, soil HONO emissions could be remarkably enhanced by agricultural nitrogen fertilization, which was not considered in this study because field HONO emission flux measurement is still unavailable.

The DMA8 O₃ simulations during the wheat growing season (53.8 ppb) for case 6S still underestimated the observations (57.4 ppb) by 3.6 ppb after considering the potential HONO sources. To better improve the O₃ simulations, we increased VOC emissions by 15% or decreased NO_x emissions by 15% for the whole region during the wheat growing season, and the results are presented in **Fig. S11**. Although DMA8 O₃ mixing ratios were systematically elevated by ~2–3 ppb for these cases (base_115VOCs and 6S_115VOCs, and base_85NO_x and 6S_85NO_x) with increasing VOC emissions or decreasing NO_x emissions, DMA8 O₃ enhancements among the three emissions scenarios (6S minus Base, 6S_115VOCs minus Base_115VOCs and 6S_85NO_x minus Base_85NO_x) were minor (<0.3ppb), suggesting that the RYL differences induced by the potential HONO sources based on the different VOCs or NO_x emission scenarios were small (**Fig. S12**).

Discussion

203 This study, for the first time, evaluated the crop yield loss induced by the potential HONO sources on
204 a regional scale, and helped to better understand the crop yield losses caused by O₃ pollution regionally
205 and globally. Very limited HONO observations suggest that more field observations of HONO in rural
206 and remote areas are urgently needed to further understand the formation mechanisms of HONO and
207 its impacts on the atmospheric environment and crop yields. HONO mixing ratios were positively
208 correlated with NO_x concentrations²⁹, however, highly non-linear relationship existed between O₃ and
209 VOCs/NO_x mixing ratios (**Fig. 5**). Higher NO_x mixing ratios can elevate HONO mixing ratios, which
210 can promote O₃ formation, yet higher NO_x mixing ratios would also terminate radicals cycling or titrate
211 with O₃ directly, result in O₃ decreasing when VOCs are insufficient³⁰.

212 The commercial losses of wheat and maize were estimated according to RYL and the total crop
213 yields obtained from the National Bureau of Statistics of China. The wheat and maize yields in NCP
214 (a rough estimation by using the sum of Anhui, Henan, Jiangsu, Shandong, Hebei, Beijing and Tianjin)
215 in 2016 reached 9.82×10^7 and 6.42×10^7 tons (**Table S3**), respectively, and the corresponding losses
216 reached 1.26×10^7 (mean wheat RYL of 11.4%) and 2.19×10^6 (mean maize RYL of 3.3%) tons,
217 respectively, due to the potential HONO sources. The purchase price was ~ US\$0.3 kg⁻¹ for wheat and
218 maize in 2016, and the commercial losses reached ~ US\$3.78 billion for wheat and ~ US\$0.66 billion
219 for maize, i.e., a crop loss of ~ US\$4.44 billion was induced by the potential HONO sources in NCP
220 in 2016 (**Fig. 5**).

Fig. 5 | The key mechanism of ozone (O_3) formation induced by nitrous acid (HONO) and the relative yield losses induced by potential HONO sources in North China Plain in 2016 for wheat and maize.

The enhancement of O₃ induced by the six potential HONO sources was found in this study and many other regions (**Table S2**), implying that considerable crop yield losses induced by potential HONO sources may occur globally, and more efforts are needed to better understand HONO sources and their impacts.

Methods

Crop yield loss evaluation methods

Five cumulative metrics for total ozone exposure (AOT40, M7, M12, SUM06 and W126) were used in this work, and they are defined as follows:

$$AOT40(ppm \cdot h) = \sum_{i=1}^n ([C_{O3}]_i - 0.04) \quad C_{O3} \geq 0.04 ppm \quad (E1)$$

$$M7(\mathbf{ppb}) = \frac{1}{n} \sum_{i=1}^n [C_{O3}]_i \quad i \text{ is from } 9:00 \text{ to } 15:59 \quad (E2)$$

$$\mathbf{M12(ppb)} = \frac{1}{n} \sum_{i=1}^n [C_{O_3}]_i \quad i \text{ is from } 8:00 \text{ to } 19:59 \quad (\text{E3})$$

$$SUM06(ppb) = \sum_{i=1}^n [C_{O_3}]_i \quad C_{O_3} \geq 60ppb \quad (E4)$$

$$W126(ppm \cdot h) = \sum_{i=1}^n \left[\frac{C_{O_3}}{1 + 4403 \exp(-126 * C_{O_3})} \right]_i \quad C_{O_3} \geq 0ppm \quad (E5)$$

AOT40 is the sum of differences between hourly O₃ mixing ratios and 40 ppb when O₃ mixing ratios (C_{O₃}) are > 40 ppb during the crop growing season¹⁸; M7 and M12 are the 7 h- and 12 h-averaged daytime surface O₃ during the crop growing season¹⁷; SUM06 emphasizes both exposure duration and peak O₃³¹, and W126 provides smaller weight factors to lower O₃ mixing ratios and larger weight factors to higher O₃ mixing ratios based on a weighting function¹⁵. In this study, the reported ER functions were collected with different O₃ exposure metrics, and these functions were independently derived and can be adopted to evaluate the ranges and uncertainties of the relative yield (RY) and relative yield loss (RYL). In total, nine ER functions for wheat and five ER functions for maize (Table 1) were applied with the five metrics described above.

Table. 1 Exposure-Response (ER) equations used to calculate the relative yield (RY) for wheat and maize.

Wheat	Abbrev	Ref	Maize	Abbrev	Ref
RY=0.99-0.0111×AOT40	AOT40_1	32	RY=1.02-0.0036×AOT40	AOT40_5	18
RY=0.99-0.0161×AOT40	AOT40_2	18	RY=1.03-0.0067×AOT40	AOT40_6	36
RY=0.99-0.0228×AOT40	AOT40_3	33	RY=exp[-(M7/158.0) ^{3.69}]/exp[-(25.0/158.0) ^{3.69}]	M7_2	17
RY=exp(-0.0255×AOT40)	AOT40_4	33	RY=exp[-(M12/124) ^{2.83}]/exp[-(20.0/124) ^{2.83}]	M12	14
RY=exp[-(M7/137) ^{2.34}]/exp[-(25./137) ^{2.34}]	M7_1	17	RY=exp[-(W126/93.7) ^{3.392}]	W126_3	31
RY=1.00-0.017×SUM06	SUM06_1	34	RYL is calculated as below: RYL= 1 - RY		
RY=exp[-(SUM06/52.32) ^{2.176}]	SUM06_2	31			
RY=exp[-(W126/51.2) ^{1.747}]	W126_1	15			
RY=exp[-(W126/53.4) ^{2.367}]	W126_2	35			

Model setup

The improved WRF-Chem model version 3.7.1 was used in this study, and the adopted physical and chemical schemes are shown in **Table S8**. Two domains were used. Domain one covers East Asia with a horizontal resolution of 81 km and contains 82×64 grid cells, and domain two covers NCP and its surrounding area with a horizontal resolution of 27 km, containing 45×45 grid cells (**Fig. 6**). Anthropogenic emissions for whole East Asia were taken from the MIX emission inventory (<http://www.meicmodel.org/>) for 2010³⁷. The MIX inventory included both gaseous and aerosol species, i.e., SO₂, NO_x, CO, VOCs, NH₃, PM₁₀, PM_{2.5}, BC, OC and CO₂, and was provided monthly by five sectors (power, industry, residential, transportation and agriculture) at a resolution of 0.25°×0.25°. VOCs emissions were speciated into model-ready inputs according to the MOZART chemical mechanism to build the WRF-Chem emission files. In this study, anthropogenic emissions in China in 2016 were replaced by employing the MEIC (Multi-resolution Emission Inventory for China) developed by Tsinghua University. The NH₃ emissions in China were from Dong et al.³⁸, biomass burning emissions were from Huang et al.³⁹ and biogenic emissions were calculated using the Model of Emissions of Gases and Aerosols from Nature (MEGAN)⁴⁰. The 1° × 1° final reanalysis data (FNL)⁴¹ from the National Centers for Environmental Prediction (NCEP) were used in this study to obtain the meteorological initial and boundary conditions (every 6 h). The global simulations of MOZART-4 (<https://www.acom.ucar.edu/wrf-chem/mozart.shtml>) were used as the chemical initial and boundary conditions (every 6 h) for this study.

Fig. 6 Domains of the WRF-Chem model (left panel), and the locations of the HONO observation sites (the red dot is the rural site in the cropland of Wangdu, and the navy-blue dot is the urban site in Beijing), NO₂ and O₃ observation sites (69 deep pink dots), and meteorological observation sites (410 black dots) in domain 2 (right panel). The white rectangle in the right panel represents the core region of the North China Plain (NCP) we concerned.

According to the actual wheat-maize rotation system in NCP in 2016, the growing seasons affected by O₃ were defined as the period from March 01 to May 31 (92 days) for wheat and from July 01 to September 30 (92 days) for maize. Two simulation cases (Base and 6S, **Table S9**) were conducted for each of the 6 months. Other 15 additional cases (**Table S9**) were performed to discuss the uncertainty of VOC emissions in the O₃ simulations (cases base_115VOCs and 6S_115VOCs), the uncertainty of NO_x emissions in the O₃ simulations (cases base_85NO_x and 6S_85NO_x), the relative contribution of each HONO source to the HONO simulations (cases A, B, C, D, E and Nit_30), and the uncertainty of α and $J_{\text{nitrate}}/J_{\text{HNO}_3}$ ratios in the HONO simulations (cases 6S_100 α , 6S_200 α , Nit_1, Nit_7, Nit_30 and Nit_120). All the simulation cases were conducted with a spin-up period of 7 days.

Potential HONO sources considered in this study

The base case only considered the key homogeneous formation of HONO (NO + OH → HONO),

287 whereas case 6S contained six potential HONO sources, i.e., traffic emissions ⁴², soil emissions ⁴³,
 288 indoor emissions ⁷, inorganic nitrate photolysis in the atmosphere (R9) ⁴⁴, and nitrogen dioxide (NO₂)
 289 heterogeneous reactions on aerosol and ground surfaces ⁴⁵.

291 The traffic emission was calculated by a HONO/NO_x ratio of 0.8% ⁴²; the soil emissions were chosen
 292 with low emission fluxes ^{7,8,43} and the reason for this choice is provided in Zhang et al. ⁷. The indoor
 293 emission source had a small influence only in urban areas with an emission rate of 2.36 ngNm⁻²s⁻¹ ⁴⁰.
 294 Nitrate photolysis was computed by a J_{nitrate}/J_{HNO₃} ratio of 30 ^{9,25} (ratios of 1, 7 and 120 were conducted
 295 for the uncertainty analysis), where J_{nitrate} and J_{HNO₃} denote the photolysis frequency of nitrate and gas
 296 nitric acid, respectively. The NO₂ heterogeneous reactions were parameterized according to the work
 297 of Li et al. ⁴ and Liu et al. ⁴⁶, and both studies considered the photo-enhanced processes on
 298 ground/aerosol surfaces ⁴⁷⁻⁴⁹. In this study, the uptake coefficient (γ) of NO₂ on aerosol and ground
 299 surfaces, and the yield (f) of HONO from NO₂ reaching the ground surface ($f \leq 1$) were improved from
 300 the previous work ^{4,7,46} and calculated by (E6) and (E7), where SR denotes solar radiation (W m⁻²), α
 301 is an adjusted factor set as 300 W m⁻² ($\alpha = 100$ or 200 W m⁻² for the uncertainty analysis), and γ and f
 302 become continuous functions during the whole day. Assuming that the intensity of SR reached 900 W
 303 m⁻² around noon, the maximum values of γ and f reached 2.0×10⁻⁵ and 0.40, respectively, which are
 304 comparable with previous studies ^{46,50}.

$$305 \quad \gamma = 5 \times 10^{-6} \times \left(1 + \frac{SR}{\alpha}\right) \quad (E6)$$

$$306 \quad f = 0.10 \times \left(1 + \frac{SR}{\alpha}\right) \quad (E7)$$

307 **Observed data**

Two field measurements of HONO were collected in the summer of 2016, including a rural site and an urban site. The rural site was in an agricultural field in Wangdu County (38.70°N, 115.25°E), which is a typical site surrounded by agricultural fields with a winter wheat-summer maize rotation in NCP⁵¹. A stripping coil-ion chromatograph (SC-IC) method was used for the HONO measurement from July 09 to August 12, with a time resolution of 1 h and a detection limit of 20 ppt⁵². The urban site was at the campus of Beijing Normal University (39.96°N, 116.36°E), using the long-path liquid absorption photometer (LOPAP)⁵³ with a time resolution of 1 h and a detection limit of 20 ppt. Ground O₃ and NO₂ mixing ratios were obtained from <https://quotsoft.net/air/>, issued by the China Ministry of Ecology and Environment; nitrate observations were absent during the study period; and surface meteorological observations were obtained from the National Climatic Data Center, China Meteorological Administration⁵⁴. A total of 69 O₃/NO₂ observation sites and 410 meteorological observation sites were used, and their locations are shown in the right panel of **Fig. 6**.

320

321 **Definition of statistical measures**

The statistical measures used in this study including the mean bias (MB), normalized mean bias (NMB), root mean square error (RMSE) and index of agreement (IOA). The MB, NMB, RMSE and IOA are calculated as follow:

$$325 \quad \text{Mean Bias (MB)} = \frac{\sum_{i=1}^N (P_i - O_i)}{N}$$

$$326 \quad \text{Normalized Mean Bias (NMB)} = \frac{\sum_{i=1}^N (P_i - O_i)}{\sum_{i=1}^N O_i} \times 100\%$$

$$327 \quad \text{Root Mean Square Error (RMSE)} = \sqrt{\frac{\sum_{i=1}^N (P_i - O_i)^2}{(N-1)}}$$

$$328 \quad \text{Index Of Agreement (IOA)} = 1 - \frac{\sum_{i=1}^N (O_i - P_i)^2}{\sum_{i=1}^N (|P_i - \bar{O}| + |O_i - \bar{O}|)^2}$$

Where P_i represents the simulated data and O_i represents the observed data. N means the number of data pairs. $\bar{O}$ is the mean of observations.

Model performance for meteorological factors and NO₂

The statistical values of the 410-site-averaged simulations of air temperature, relative humidity and wind speed were comparable with those of previous studies (Table S10), and the wind direction biases within 45° were over 50% in both seasons (Table S10). Overall, the simulations of the meteorological variables are reasonable.

The 69-site-averaged hourly and diurnal variations of NO₂ in the two growing seasons were well simulated (Fig. S13&S14). The mean NO₂ for the base and 6S cases and the observations in the wheat/maize growing seasons were 21.76/20.76, 20.77/19.71 and 21.40/17.43 ppb, respectively. The nighttime NO₂ for the 6S case was closer to the observations compared with the base case after considering the heterogeneous consumption of NO₂ leading to HONO formation (Fig. S14). Nighttime NO₂ overestimation could be related mainly to the uncertainty in the NO_x emissions (Fig. S13&S14), which probably caused the overestimation of nighttime HONO by ~0.2–0.5 ppb at both sites (Fig. 1).

Calculation of RYL_{base}, RYL_{6S} and RYL_{Obs}

$$RYL_{base} = 1 - RY_{base} \quad (E8)$$

$$RYL_{6S} = 1 - RY_{6S} \quad (E9)$$

$$RYL_{Obs} = 1 - RY_{Obs} \quad (E10)$$

where RY_{base} , RY_{6S} and RY_{Obs} are calculated by applying the simulated (base and 6S cases) and the observed O_3 mixing ratios, respectively, into the ER equations. The relative contribution in the lower panel of **Fig. 4** is defined as below:

$$\text{Relative contribution} = \frac{(RYL_{6S} - RYL_{base})}{RYL_{Obs}} \times 100\% \quad (E11)$$

Competing interests

The authors declare no competing interests.

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Figures

Figure 1

Comparison of simulated (Base and 6S cases) and observed hourly and diurnal HONO mixing ratios at the rural (a&c) and urban (b&d) sites in summer of 2016, and comparison of simulated (Base and 6S cases) and observed 69-site-averaged diurnal O₃ in the North China Plain during the wheat (e) and maize (f) growing seasons in 2016.

Figure 2

Daily maximum 8-h (10:00–17:59) surface O₃ simulations for the base (a1/a2) and 6S cases (b1/b2) and the enhancements (c1/c2) induced by the potential HONO sources during the wheat/maize growing season. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 3

Box plots of the relative yield loss (RYL) induced by the potential HONO sources calculated by the 14 exposure-response (ER) equations in NCP in 2016.

Figure 4

The 69-site-averaged relative yield loss (RYL) values calculated by using 14 Exposure-Response (ER) equations for the base (RYL_{base}, light blue histogram) and 6S (RYL_{6S}, light red histogram) cases and observed O₃ (RYL_{obs}, gray histogram) for wheat (a) and maize (b); and the relative contribution of the RYL caused by the enhanced O₃ (O₃ simulations of the 6S case minus those of the base case) to the actual RYL (RYL_{obs}) for wheat (c) and maize (d).

Figure 5

The key mechanism of ozone (O_3) formation induced by nitrous acid ($HONO$) and the relative yield losses induced by potential $HONO$ sources in North China Plain in 2016 for wheat and maize.

Figure 6

Domains of the WRF-Chem model (left panel), and the locations of the HONO observation sites (the red dot is the rural site in the cropland of Wangdu, and the navy-blue dot is the urban site in Beijing), NO₂ and O₃ observation sites (69 deep pink dots), and meteorological observation sites (410 black dots) in domain 2 (right panel). The white rectangle in the right panel represents the core region of the North China Plain (NCP) we concerned. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

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