Measurement Report: Elevated excess-NH₃ can promote the redox reaction to produce HONO: Insights from the COVID-19 pandemic

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Abstract

The incongruity between atmospheric oxidizing capacity and NOx emissions during the COVID-19 pandemic remains puzzling. Here, we show evidence from field observations of ten sites in China that there was a noticeable increase in NH3 concentrations during the COVID-19 pandemic. In addition to the meteorological conditions, the significant decrease in sulfate and nitrate concentrations enhanced the portioning of NH4+ to NH3. Such conditions enable enhanced particle pH values, which in turn accelerate the redox reactions between NO2 and SO2 to form HONO. This mechanism partly explains the enhanced atmospheric oxidizing capacity during the pandemic and highlights the importance of coordinating the control of SO2, NOx, and NH3 emissions.
1. Introduction

Atmospheric oxidizing capacity (AOC) is an important parameter that affects the formation of secondary aerosols and O$_3$ (Li et al., 2021a; Wang et al., 2023b). Identifying the factors influencing AOC is crucial for further reducing particulate matter and O$_3$ pollution. During the COVID-19 pandemic, unprecedented control measures were implemented, resulting in significant reductions in emissions from mobile traffic and stationary industry sources (Zheng et al., 2020; Wang et al., 2020a; Tian, 2020). However, studies have shown a surprising increase in AOC during this period (Huang et al., 2021a; Li et al., 2023; Liu et al., 2021; Wang et al., 2021; Zheng et al., 2020). Multiple studies have indicated that the sharp decrease in nitrogen oxide (NO$_x$) emissions leads to a substantial increase in O$_3$, as well as daytime OH and HO$_2$ radicals, and nighttime NO$_3$ radicals, subsequently resulting in an overall increase in AOC (Huang et al., 2021a; Li et al., 2023; Liu et al., 2021; Zheng et al., 2020). However, the exact relationship between NO$_x$ and AOC remains unclear.

Nitrous acid (HONO) is a critical precursor of OH radicals, contributing to more than 43–50% of OH production (Alicke, 2003) and exerting a strong influence on AOC (Zhang, 2023). Various sources of atmospheric HONO have been identified, including combustion processes (e.g., vehicle emissions) (Kramer et al., 2020; Liao et al., 2021a; Li et al., 2021b), direct emissions from soil (Su and Zhang, 2011; Oswald et al., 2013; Meusel et al., 2018), homogeneous reactions between NO and OH radicals (Pagsberg, 1997; Atkinson and Rossi, 2004), heterogeneous reactions of NO$_2$ on aerosols and ground surfaces (Zhang et al., 2020a; McFall et al., 2018; Liu et al., 2014; Liu et al., 2020a), and photolysis of nitrate (Spataro and Ianniello, 2014; Scharko et al., 2014; Romer et al., 2018; Ye et al., 2017; Shi et al., 2021).

During the pandemic control periods, there was a substantial reduction in vehicle traffic flow and industrial emissions, leading to a decrease of more than 60% in NO$_x$ emissions in eastern China (Huang et al., 2021a). It was initially expected that the concentration of HONO would also decrease proportionally. However, Liu et al. observed that the decrease in HONO
concentration during the pandemic period was only 31%, which was lower than the reductions in NO (62%) and NO\textsubscript{2} (36%) (Liu et al., 2020b). Furthermore, it is worth noting that the concentration of HONO during the COVID-19 pandemic in 2020 was higher compared to the levels observed during the corresponding period in 2021 (Luo et al., 2023). This finding suggests the existence of a considerable unknown source of HONO during the COVID-19 pandemic.

Ammonia (NH\textsubscript{3}) is a significant alkaline gas in the atmosphere that plays a crucial role in the atmospheric nitrogen cycle (Gu et al., 2022; Xu et al., 2020; Gong et al., 2011). Several studies have indicated that NH\textsubscript{3} can promote the formation of HONO by promoting the hydrolysis of NO\textsubscript{2} (Xu et al., 2019) or the redox reaction of NO\textsubscript{2} with SO\textsubscript{2} (Liu et al., 2023). Moreover, previous research has shown that NH\textsubscript{3} concentrations in the atmosphere, particularly in rural areas, significantly increased during the pandemic (Xu et al., 2022). Consequently, the rise in NH\textsubscript{3} may contribute to the enhanced formation of HONO and subsequently enhance AOC. Unfortunately, there is currently a lack of research on the relationship between enhanced NH\textsubscript{3} and AOC during the COVID-19 pandemic period.

To address this, online observational data on particulate matter composition, gaseous pollutants, and meteorological conditions from ten sites in China before and during the COVID-19 pandemic period were analyzed to investigate the variation in NH\textsubscript{3} concentrations and particle pH and explore the promoting effect of increased pH values on HONO formation. To the best of our knowledge, this is the first study to discuss the reasons for the increase in AOC during the pandemic from the perspective of the influence of NH\textsubscript{3} on HONO.

2. Materials and methods

2.1 Observation sites

Online measurements were conducted at four urban and six rural sites from January 1 to February 29, 2020, including Sanmenxia (U-SMX), Zhoukou (U-ZK), Zhumadian (U-ZMD),
and Xinyang (U-XY), as well as rural locations including Anyang (R-AY), Xinxiang (R-XX), Jiaozuo (R-JZ), Shangqiu (R-SQ), Nanyang (R-NY), and Puyang (R-PY). Descriptions and the spatial distribution of these ten sites can be found in Table S1 and Figure S1 of Supplementary Material.

2.2 Measurements

The aerosol and gas monitor (MARGA, Metrohm, Switzerland) was used to analyze the hourly water-soluble ions (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, and SO₄²⁻) in PM$_{2.5}$, as well as gaseous species (NH₃, HNO₃, HCl, and HONO) at ten sampling sites. The MARGA instrument is widely used (Chen et al., 2017; Stieger et al., 2019; Twigg et al., 2022). A detailed description of the instrument and QA/QC can be found in Text S1. In brief, the atmospheric sample passes through a PM$_{2.5}$ cut-off head, and both particles and gases enter a wet rotating dissolution device for diffusion. Subsequently, the particles in the sample undergo hygroscopic growth and condensation in an aerosol supersaturated vapor generator, followed by collection and ion chromatographic analysis. The gases in the sample are oxidized by H₂O₂ in the dissolution device, absorbed into a liquid solvent, and then entered the gas sample collection chamber for ion chromatographic quantification. The range of minimum detection limits for water-soluble ions was between 0.002 μg/m$^3$ (Cl⁻) to 0.081 μg/m$^3$ (NH₄⁺). Previous works have shown that HONO observations measured using this system agree well with other observational services, a detailed description of HONO and its uncertainty can be found in Text S3. Overall, the limit of detection for HONO was 4 pptv and the uncertainty was estimated to be ±20%. In addition, Uncertainties of 20% are assumed for the detection of NH$_3$ and NH$_4^+$, while uncertainties of 10% are assumed for other components (Wang et al., 2020b; Wang et al., 2022).

The data for NO$_2$ and SO$_2$ were obtained from a series of instruments provided by Thermo Fisher Scientific (USA). The hourly concentrations of organic carbon (OC) in PM$_{2.5}$ were analyzed using a carbon analyzer (Model 4, Sunset Laboratory., USA). A detailed description of the NO$_2$, SO$_2$, and carbon analyzer can be found in Text S2. The smart weather
stations (LUFFTWS500, Sutron, Germany) were utilized for synchronized observation of meteorological parameters including temperature and relative humidity (RH).

2.3 Data analysis.

2.3.1 pH prediction.

The thermodynamic model ISORROPIA-II was used to estimate the pH value of the particles (Fountoukis, 2007) by inputting RH, temperature, K+, Ca2+, Mg2+, total ammonia (TNH = NH4+ + NH3), total sulfuric acid (TH2SO4, SO42−), total sodium (TNa, Na+), total chlorine (TCl, Cl−), and total nitrate (TNO3 = NO3− + HNO3). The ISORROPIA model calculated the particle hydrate ion concentration per volume of air (H_air+ + AWC_inorg) and particulate water associated with inorganic matter (AWC_inorg). The aerosol pH value was calculated using the following equation (Bougiatioti et al., 2016):

\[ \text{pH} = -\log_{10} \left( H_{aq}^- + \frac{1000H_{aq}^+}{\text{AWC}_{\text{inorg}} + \text{AWC}_{\text{org}}} \right) \]  

where the modeled concentrations for AWC_inorg and H_aq+ are μg/m^3, and AWC_org is the particle water associated with the organic matters predicted using the following method:

\[ \text{AWC}_{\text{org}} = \frac{m_{\text{OC}}}{\rho_{s}} \left( \frac{k_{\text{org}}}{\text{RH} - 1} \right) \]  

where \( m_{\text{OC}} \) is the mass concentrations of organic matter (OC×1.6), \( \rho_{s} \) is the organic density (1.35 g cm^{-3}), and \( k_{\text{org}} \) is the organic hygroscopicity parameter (Liu et al., 2017; Wang et al., 2023a). \( k_{\text{org}} \) is the organic hygroscopicity parameter and depends on organic functionality, water solubility, molecular weight, and oxidation level. Han (Han et al., 2022) has reported that the \( k_{\text{org}} \) generally increased with O: C ratios, with a range of 0 – 0.3 for 23 organics, including carboxylic acids, amino acids, sugars, and alcohols. Wang et.al(Wang et al., 2023a) estimated that the uncertainties of \( k_{\text{org}} \) value (0.06) for pH only lead to –1–3% errors, which can be neglected. Therefore, the value of 0.06 was selected in this paper. The model has two calculation modes: the forward mode and reverse mode, and the aerosol dissolution systems.
can be set to simulate a metastable state (aqueous phase) or stable state (aqueous and solid phase). Studies have shown that the forward mode is less affected by instrument measurement errors than the reverse mode (Ding et al., 2019; Song et al., 2018). Additionally, the minimum average RH of about 55% was recorded during the sampling period at the ten sites. Thus, ISORROPIA-II was run in the forward model for the aerosol system in the metastable condition.

2.3.2 The HONO source analysis

The source rates of HONO include direct emission ($P_{em}$), homogeneous reaction of NO and •OH ($P_{OH\cdot NO}$), heterogeneous reaction of NO$_2$ on the ground ($P_{ground}$) and aerosol ($P_{aerosol}$), photo-enhanced heterogeneous reaction of NO$_2$ on the ground ($P_{ground\cdot hv}$) and aerosol ($P_{aerosol\cdot hv}$), nitrate photolysis ($P_{nitrate}$), and unknown source ($P_{unknown}$). The detailed methodology for its calculation is described in the Supplementary Material (Text S4).

2.3.3 Production rate of HONO through redox reaction of NO$_2$ with SO$_2$.

The redox reaction of NO$_2$ with SO$_2$ ($R_1$) is considered a crucial potential source of high concentrations of HONO in Northern China (Cheng et al., 2019; Wang et al., 2016):

$$S(IV) + 2NO_2 + H_2O \rightarrow S(VI) + 2H^+ + 2NO_2^- \quad (R_1)$$

The rate expression for reaction ($R_1$) was estimated to:

$$\frac{d[S(\text{VI})]}{dt} = k_1[NO_2][S(\text{VI})], \quad (2.3)$$

The rate constant $k_1$ value is pH dependent, e.g., for pH 5, $k_1 = (1.4\times10^5+1.24\times10^7)/2$ M$^{-1}$ s$^{-1}$. For $k_1$ values under other pH conditions and other related information, please refer to Text S5, Table S2, and S3.
3. Results and discussion

3.1 Variations of NH$_3$, NH$_4^+$ and TNH$_x$.

The temporal variations of NH$_3$, NH$_4^+$, and TNH$_x$ at 10 sampling sites in the pre-COVID-19 pandemic period (PC, January 1 to 23, 2020) and during the COVID-19 pandemic period (DC, January 24 to February 29, 2020) are presented in Figure 1, with their average concentration listed in Table 1. In general, rural sites exhibited higher concentrations of NH$_3$, NH$_4^+$, and TNH$_x$ compared to urban sites, except for the R-NY site. This finding is consistent with previous studies conducted in Zhengzhou (Wang et al., 2020b), Shanghai (Chang et al., 2019), and Quzhou (Feng et al., 2022a), owing to the intense agricultural ammonia emissions. The highest concentrations of NH$_3$ and TNH$_x$ were recorded at site R-JZ, with average values of 25.3 ± 11.5 and 40.8 ± 20.1 μg/m$^3$, respectively. Site R-AY had the highest NH$_4^+$ concentration, measuring 19.3 ± 12.9 μg/m$^3$. Note that the current study area exhibited higher NH$_3$ levels compared to other regions (Table S4), which probably was attributed to the highest NH$_3$ emissions of Henan Province in China, primarily from nitrogen fertilizer application and livestock farming (Wang et al., 2018; Ma, 2020). Compared to the PC, NH$_3$ concentrations increased in the DC at all sites. Notably, rural sites experienced more significant increases in NH$_3$ concentrations than urban sites, which is similar to the trend in Shanghai (Xu et al., 2022). The largest increases in NH$_3$ concentrations were observed at R-SQ (71%, 7.3 μg/m$^3$) and U-ZK (37%, 4.8 μg/m$^3$) for rural and urban sites, respectively. In contrast, the concentrations of NH$_4^+$ and TNH$_x$ decreased in the DC with the largest reduction at rural site R-PY (51%, 12.9 μg/m$^3$) and urban site U-ZMD (48%, 9.3 μg/m$^3$). Regarding TNH$_x$, rural sites exhibited larger reductions, with site R-SQ experiencing the largest decrease of 37% (4.7 μg/m$^3$).
Figure 1. Temporal variations of a. NH₃, b. NH₄⁺, and c. TNHₓ at the urban and rural sites before (PC) and during (DC) the COVID-19 outbreak, respectively. The shaded areas of the curve represent the maximum and minimum values.
Table 1. Changes in concentrations (mean ± standard deviation) of NH$_3$, NH$_4^+$, and TNH$_x$ at ten sites average (overall average for the period of observation), before (PC) and during (DC) the COVID-19 outbreak.

<table>
<thead>
<tr>
<th>Site</th>
<th>Substance</th>
<th>Average ($\mu$g/m$^3$)</th>
<th>PC ($\mu$g/m$^3$)</th>
<th>DC ($\mu$g/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-SMX</td>
<td>NH$_3$</td>
<td>13.8 ± 10.8</td>
<td>12.6 ± 10.1</td>
<td>14.5 ± 11.1</td>
</tr>
<tr>
<td></td>
<td>NH$_4^+$</td>
<td>10.9 ± 7.2</td>
<td>14.2 ± 7.2</td>
<td>8.8 ± 6.5</td>
</tr>
<tr>
<td></td>
<td>TNH$_x$</td>
<td>22.9 ± 14.1</td>
<td>24.9 ± 14.5</td>
<td>21.7 ± 13.8</td>
</tr>
<tr>
<td>U-ZK</td>
<td>NH$_3$</td>
<td>15.6 ± 8.3</td>
<td>12.7 ± 6.5</td>
<td>17.4 ± 8.8</td>
</tr>
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<td>NH$_4^+$</td>
<td>13.6 ± 9.3</td>
<td>19.1 ± 8.4</td>
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<tr>
<td></td>
<td>TNH$_x$</td>
<td>28.6 ± 13.7</td>
<td>30.9 ± 12.8</td>
<td>27.1 ± 14.0</td>
</tr>
<tr>
<td>U-ZMD</td>
<td>NH$_3$</td>
<td>13.1 ± 8.4</td>
<td>11.6 ± 8.2</td>
<td>14.0 ± 8.4</td>
</tr>
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<td>NH$_4^+$</td>
<td>13.9 ± 9.8</td>
<td>19.6 ± 10.3</td>
<td>10.3 ± 7.5</td>
</tr>
<tr>
<td></td>
<td>TNH$_x$</td>
<td>25.7 ± 14.6</td>
<td>30.3 ± 15.1</td>
<td>22.8 ± 13.5</td>
</tr>
<tr>
<td>U-XY</td>
<td>NH$_3$</td>
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<td>5.7 ± 4.0</td>
<td>7.9 ± 4.3</td>
</tr>
<tr>
<td></td>
<td>NH$_4^+$</td>
<td>11.0 ± 7.7</td>
<td>15.4 ± 7.6</td>
<td>8.3 ± 6.5</td>
</tr>
<tr>
<td></td>
<td>TNH$_x$</td>
<td>17.6 ± 9.8</td>
<td>20.6 ± 10.1</td>
<td>15.7 ± 9.2</td>
</tr>
<tr>
<td>R-AY</td>
<td>NH$_3$</td>
<td>19.0 ± 8.4</td>
<td>17.9 ± 8.3</td>
<td>19.7 ± 8.4</td>
</tr>
<tr>
<td></td>
<td>NH$_4^+$</td>
<td>19.3 ± 12.9</td>
<td>26.4 ± 13.7</td>
<td>15.0 ± 10.3</td>
</tr>
<tr>
<td></td>
<td>TNH$_x$</td>
<td>36.6 ± 18.2</td>
<td>41.7 ± 20.4</td>
<td>33.4 ± 16.0</td>
</tr>
<tr>
<td>R-XX</td>
<td>NH$_3$</td>
<td>21.7 ± 10.2</td>
<td>18.1 ± 9.3</td>
<td>23.8 ± 10.1</td>
</tr>
<tr>
<td></td>
<td>NH$_4^+$</td>
<td>15.9 ± 10.4</td>
<td>20.6 ± 11.0</td>
<td>13.0 ± 8.8</td>
</tr>
<tr>
<td></td>
<td>TNH$_x$</td>
<td>34.9 ± 17.0</td>
<td>35.1 ± 18.8</td>
<td>34.8 ± 15.8</td>
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<tr>
<td>R-PY</td>
<td>NH$_3$</td>
<td>19.8 ± 9.4</td>
<td>16.8 ± 8.1</td>
<td>21.7 ± 9.6</td>
</tr>
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<td></td>
<td>NH$_4^+$</td>
<td>17.4 ± 11.8</td>
<td>25.3 ± 12.6</td>
<td>12.4 ± 8.0</td>
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<td></td>
<td>TNH$_x$</td>
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<td>39.4 ± 19.8</td>
<td>32.6 ± 15.7</td>
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<tr>
<td>R-JZ</td>
<td>NH$_3$</td>
<td>25.3 ± 11.5</td>
<td>24.1 ± 11.5</td>
<td>25.9 ± 11.4</td>
</tr>
<tr>
<td></td>
<td>NH$_4^+$</td>
<td>17.3 ± 11.3</td>
<td>22.7 ± 11.6</td>
<td>14.2 ± 9.9</td>
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<td></td>
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<td>40.8 ± 20.1</td>
<td>42.9 ± 22.8</td>
<td>33.5 ± 18.2</td>
</tr>
<tr>
<td>R-SQ</td>
<td>NH$_3$</td>
<td>15.0 ± 7.9</td>
<td>10.3 ± 5.2</td>
<td>17.7 ± 7.9</td>
</tr>
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<td></td>
<td>NH$_4^+$</td>
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<td>10.3 ± 6.7</td>
</tr>
<tr>
<td></td>
<td>TNH$_x$</td>
<td>26.3 ± 13.2</td>
<td>25.5 ± 14.0</td>
<td>26.8 ± 12.7</td>
</tr>
<tr>
<td>R-NY</td>
<td>NH$_3$</td>
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<td>4.3 ± 2.7</td>
<td>6.2 ± 3.2</td>
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<td>NH$_4^+$</td>
<td>10.2 ± 6.9</td>
<td>13.3 ± 7.2</td>
<td>8.4 ± 6.1</td>
</tr>
<tr>
<td></td>
<td>TNH$_x$</td>
<td>14.8 ± 8.5</td>
<td>16.0 ± 9.5</td>
<td>14.1 ± 7.8</td>
</tr>
</tbody>
</table>

Figure 2 illustrates the spatial distribution and the diurnal variation of NH$_3$ concentrations in the ten sites before and during the pandemic. NH$_3$ concentrations in most sites exhibited a unimodal trend in PC that NH$_3$ concentrations gradually increased after sunrise, reaching a peak around noon (11:00-12:00), and then decreased to a valley around 16:00-17:00. This diurnal pattern is similar to NH$_3$ variations observed in urban areas of Houston, USA, as a
result of the natural emissions from vegetation and soil during photosynthesis (Gong et al., 2011). However, other studies have recorded a significant NH$_3$ peak during the early morning of 8:00-10:00 (Ellis et al., 2011; Meng et al., 2018; Gu et al., 2022), suggesting the influence of vehicle emissions (Gong et al., 2011; Gu et al., 2022), residual NH$_3$ mixing, soil or plant emissions (Ellis et al., 2011), and dew volatilization (Wentworth et al., 2016; Huang et al., 2021b). Therefore, the NH$_3$ in urban and rural areas of this study was less affected by NH$_3$ emissions from vehicles, different from the recent studies in megacities of China (e.g., Beijing and Shanghai)(Gu et al., 2022; Wu et al., 2023; Zhang et al., 2020b). In addition to the transport from agricultural emissions, urban NH$_3$ in this region may originate from other non-agricultural sources, such as wastewater treatment, coal combustion, household waste, urban green spaces, and human excrement (Chang et al., 2019).

During the COVID-19 pandemic, the diurnal variation of NH$_3$ in both urban and rural sites still maintained a unimodal distribution. The peak values in urban sites remained consistent with PC levels, further demonstrating that the influence of vehicles on NH$_3$ in urban areas was limited. Notably, the peak time of NH$_3$ in rural sites shifted 1–2 hours earlier compared to the trend in PC. Ammonia in rural areas primarily originates from nitrogen fertilizer application, livestock, and poultry breeding (Feng et al., 2022a; Meng et al., 2018), which are significantly influenced by temperature and RH (Liu et al., 2023). Table S5 and Figure S2 reveal that the increased temperatures and decreased RH at rural sites in the PC, could accelerate the evaporation of NH$_3$ and thus potentially lead to earlier peak NH$_3$ concentrations.
Figure 2. Daily variation of ammonia concentration at ten sites before (PC) and during (DC) the COVID-19 outbreak. The green dots represent the location of ten sites and their size represent the concentration of NH₃; the upper and lower whiskers represent the maximum and minimum values, respectively.
3.2 Gas-to-particle conversion of NH$_3$

Theoretically, the emissions of NH$_3$ from agricultural sources were not influenced by the containment measures, and emissions from vehicles and industries would decrease significantly in the DC. Consequently, the concentration of NH$_3$ should decrease in the DC, which was opposite to the observed trends. The decreased NH$_4^+$ in the DC suggests that the gas-particle partitioning of NH$_3$/NH$_4^+$ may determine the elevated NH$_3$ concentrations. Meteorological parameters, including RH and temperature, play a crucial role in the gas-particle partitioning of NH$_3$ (Liu et al., 2023; Xu et al., 2020). Therefore, the higher temperature and lower RH in the DC (Table S5) favored the conversion of NH$_4^+$ to NH$_3$, resulting in a decrease in $\varepsilon$(NH$_4^+$) ([NH$_4^+$/([NH$_4^+$] + [NH$_3$])) compared to those in the PC.

NH$_3$ primarily enters particles to neutralize acidic ions (Wang et al., 2020b; Xu et al., 2020; Liu et al., 2017; Ye et al., 2011; Wells, 1998). Accordingly, the concentrations of required ammonia (Required-NH$_3$) and excess ammonia (Excess-NH$_3$) were calculated based on the acidic substances as follows (Wang et al., 2020b):

$$\text{TNH}_3 = 17 \times \left( \frac{[\text{NH}_4^+]}{18} + \frac{[\text{NH}_3]}{17} \right)$$  \hspace{1cm} (3.1)

$$\text{Required-NH}_3 = 17 \times \left( \frac{[\text{SO}_4^{2-}]}{48} + \frac{[\text{NO}_3^-]}{63} + \frac{[\text{Cl}^-]}{35.5} + \frac{[\text{HNO}_3]}{64} + \frac{[\text{HCl}]}{36.5} \right)$$

$$- 17 \times \left( \frac{[\text{Na}^+]}{23} + \frac{[\text{K}^+]}{39} + \frac{[\text{Ca}^{2+}]}{20} + \frac{[\text{Mg}^{2+}]}{12} \right)$$  \hspace{1cm} (3.2)

$$\text{Excess-NH}_3 = \text{TNH}_3 - \text{Required-NH}_3$$  \hspace{1cm} (3.3)

Where [W] represents the concentration of the substance ($\mu$g/m$^3$).

The significant linear fitting ($R^2$ is greater than 0.96, and the slope is close to 1) in Figure S3 demonstrates that the anions and cations at each site are close to the equilibrium state. Therefore, the organic acids in PM$_{2.5}$ had less effect on NH$_3$ and NH$_4^+$, and were not considered in formula 3.2.

As shown in Figure 3 and Table S6, compared to those in the PC, the
concentration of Required-NH₃ in the DC significantly decreased (ranging from 37% at site R-JZ to 58% at site R-PY), while the concentration of Excess-NH₃ increased (ranging from 9% at site R-AY to 78% at site R-SQ). The reduction in the concentrations of sulfate and nitrate (Figure S4) was responsible for the decrease in the concentration of Required-NH₃. To sum up, in addition to meteorological conditions, the substantial reduction in anthropogenic emissions of SO₂, NOₓ, and other pollutants in the DC has led to a decrease in acidic substances (e.g., sulfate and nitrate) in particles, in turn, resulting in more gas-phase NH₃ concentration remaining in the atmosphere.

Figure 3. Box diagram of changes in Required-NH₃ at ten sites before (PC) and during (DC) the COVID-19 outbreak. In each box, the top, middle, and bottom lines represent the 75, 50, and 25 percentiles of statistical data, respectively; the upper and lower whiskers represent the 90 and 10 percentiles of statistical data, respectively.
3.3 Particle pH before and during COVID-19

Previous studies have consistently reported that the concentration of Excess-NH₃ is the primary factor influencing the pH value of particles (Liu et al., 2023; Wang et al., 2020b). Therefore, the U-ZK (4.3 μg/m³) and R-PY (7.5 μg/m³) with the largest increase in Excess-NH₃ concentration (Table S6) for urban and rural sites respectively were selected to investigate the changes in particle pH value before and during the pandemic. The pH values at U-ZK and R-PY were 4.7 and 4.8 in the PC, respectively, which were close to the values in previous studies (Table S7). The higher pH values at the rural site than those in the urban site can be attributed to the higher concentration of Excess-NH₃ in rural areas.

Note that Figure 4 suggests that the particle pH increased in the DC, with an increase of 0.4 and 0.1 at U-ZK and R-PY, respectively. To explore the dominant factors that determine the local particle pH level and result in the high pH during the DC, sensitivity tests of pH to chemical species (i.e., TNH₃, TH₂SO₄, TNO₃, TCl, TNa, K⁺, Ca²⁺, and Mg²⁺) and meteorological parameters (i.e., T and RH) were performed. A given range for a variable for U-ZK and R-PY two sites with corresponding average values of other parameters was simulated to compare its effects on pH, the input data was collected as shown in Figure 5 and Figure S5. The uncertainty of pH is shown in Figure S6. Compared to PC, even though the decrease in TNH₃ concentration and the increase in temperature led to a decrease in pH values (0.09 at U-ZK and 0.08 at R-PY site), this effect was outweighed by the decrease in TH₂SO₄ (0.07 and 0.8 at U-ZK and R-PY site, respectively) and TNO₃ (0.05 and 0.4 at U-ZK and R-PY site, respectively) concentrations as well as the increase in K⁺ (0.03 at U-ZK and 0.2 at R-PY site) and Mg²⁺ (0.01 at U-ZK and 0.04 at R-PY site) concentrations in the DC, and resulting in an overall increase in pH values in the DC.
Figure 4. Daily variations of particle pH at a. U-ZK and b. R-PY sites before (PC) and during (DC) the COVID-19 outbreak. The upper and lower whiskers represent the maximum and minimum values, respectively.

Figure 5. Comparison of pH sensitivity (Fig. S5) to each substance by changing paraments at a. U-ZK and b. R-PY sites before (PC) and during (DC) the COVID-19 outbreak.

3.4 The influence of pH on HONO.

The observed HONO concentrations decreased by 18% and 54% at U-ZK (0.8 ppb) and R-PY (0.9 ppb) sites in the DC, respectively, compared to those (1.0 and 2.2 ppb) in the PC. Moreover, all the known HONO production sources rates including \( \text{P}_{\text{emis}} \), \( \text{P}_{\text{OH} + \text{NO}_3} \), \( \text{P}_{\text{ground}} \), \( \text{P}_{\text{ground+hv}} \), \( \text{P}_{\text{aerosol}} \), \( \text{P}_{\text{aerosol+hv}} \), and \( \text{P}_{\text{nitrate}} \) (Figure 6) show a decreasing trend from PC to DC, with the mean reductions of 38% and 80% for U-ZK and R-PY, respectively. At the U-ZK, \( \text{P}_{\text{ground+hv}} \) decreased the most (84%), while at the
R-PY, $P_{\text{nitrates}}$ had the largest decrease about 85%, which is speculated to be related to the decrease of NO$_x$ and NO$_3^-$ concentration in DC. Note that the reduction in the overall known source and almost individual sources were greater than the reduction in HONO concentrations (Figure 6 and 7), thus we hypothesized that there should be other sources capable of promoting HONO production.

The relationship between HONO concentrations and other major influences at the U-ZK and R-PY sites in the DC is displayed in Figure S7. HONO emissions were affected by temperature to some extent (Liu et al., 2020c; Liu et al., 2020b), but there was no significant positive correlation with temperature (Feng et al., 2022b), and temperatures did not exceed a maximum of 10°C during this study period, suggesting that soil emissions may not have been a major contributor to the PC HONO during this study period. In addition, the positive correlations between HONO with SO$_2$, Excess-NH$_x$, SO$_4^{2-}$, and pH indicate that the $R_1$ reaction may also form an amount of HONO and contribute to less reduction in the observed HONO concentrations.

Considering that $R_1$ mainly reacts in the liquid phase, the calculated reaction rates of $R_1$ under the conditions of RH > 60% in the PC and DC periods are illustrated in Figure 7. Despite the decrease in NO$_2$ and SO$_2$ concentrations in the DC, the
increase in particle pH, increasing HSO$_3^-$ concentration in the aqueous phase, promoted the $R_1$ reaction rates by 58% and 59% at U-ZK and R-PY (Figure 7), respectively. Consequently, the enhanced $R_1$ reaction prevented a large decrease in HONO (18% at U-ZK and 53% at R-PY) under the conditions of a significant reduction in vehicle emissions and a decline of 66% and 69% in NO$_2$ concentrations at U-ZK and R-PY, respectively.

![Figure 7. Decline ratios of a. NO$_2$, b. HONO concentration, and c. HONO production rate at U-ZK and R-PY sites before (PC) and during (DC) the COVID-19 outbreak. The center point represents the mean value, and the upper and lower whiskers represent the 95% confidence interval of the mean.](https://doi.org/10.5194/egusphere-2023-2913)

### 3.5 Uncertainty

According to sensitivity tests of pH (Figure S5) and $R_1$ (Figure S8), pH increases with the concentrations of cations (TNH$_4^+$, TNa, K$^+$, Ca$^{2+}$, and Mg$^{2+}$) and OC increasing as well as anions (TH$_2$SO$_4$, TNO$_3^-$, and TCl) concentrations, Temp, and RH decreasing. $R_1$ reaction rate increases with the concentrations of pH, AWC, NO$_2$, SO$_2$, and Pressure (Pre), while increasing as well as T (K) decreasing. Therefore, two
extreme scenarios (i.e., the maximum and minimum rate scenarios) were evaluated to estimate the uncertainty of AWC, pH, and R₁ HONO production rate based on the measurement uncertainties at the U-ZK and R-PY sites. Figure S6 suggests that the two extreme scenarios can be led to –10–7% and –71–125% uncertainties at the U-ZK site and –10–7% and –78–123% uncertainties at the R-PY site for pH and R₁, respectively.

4. Conclusions

Elevated NH₃ concentration was observed during the COVID-19 pandemic at both urban and rural sites in China. In addition to the rise in temperature and decrease in RH during the COVID-19 pandemic, which favored the conversion of NH₄⁺ to NH₃, the significant decrease in sulfate and nitrate concentrations led to the decline in Required-NH_, and was beneficial to the particle-phase NH₄⁺ portioning to gas-phase NH₃. Furthermore, under the environmental conditions of increased NH₃ concentration and decreased acidic substance concentration, the pH values increased by 0.4 and 0.1 at U-ZK and R-PY increased during the pandemic, respectively. Consequently, the high pH values accelerated the formation rate of HONO through the oxidation-reduction reaction of NO₂ with SO₂ (an increase of 58% at U-ZK and 59% at R-PY), partially compensating for the decrease in HONO concentration and its sources caused by the decline in vehicle emissions and NO₂ concentration during the COVID-19 pandemic.

5. Implications

HONO plays a crucial role as a precursor to OH radicals in the tropospheric
atmosphere (Xue, 2022). There have been significant observations of high HONO concentrations in urban areas during the daytime, leading to a growing interest in understanding its sources in atmospheric chemistry (Jiang et al., 2022; Xu et al., 2019). The heterogeneous reaction mechanism of NO$_2$ on aerosol surfaces is currently the focus of research on HONO sources, particularly in regions with elevated levels of atmospheric particulate matter, where it could potentially become a major contributor to HONO production (Zhang et al., 2022; Liao et al., 2021b). One of the pathways for heterogeneous reactions on aerosol surfaces is the redox reaction of NO$_2$ with SO$_2$. However, the significance of this reaction in HONO production in the real atmosphere is often overlooked, as it relies on the high pH of aerosols (Ge et al., 2019). In recent years, there has been increasing attention on the enhancing effect of NH$_3$ on the redox reaction, with laboratory experiments demonstrating its ability to generate substantial amounts of HONO (Ge et al., 2019). This study highlights the importance of this reaction based on actual atmospheric observations. Furthermore, numerous studies have indicated that if control over NH$_3$ emissions continues to relax while SO$_2$ and NO$_2$ emissions decrease, the particle pH in future China is expected to rise steadily (Xie et al., 2020; Song et al., 2019; Wang et al., 2020b). Consequently, the redox reaction of NO$_2$ with SO$_2$ could become a significant source of HONO in China, greatly amplifying the AOC. Therefore, it is crucial to coordinate the control of SO$_2$, NO$_x$, and NH$_3$ emissions to avoid a rapid increase in the particle pH.

**Data availability:** All the data presented in this article can be accessed through [https://zenodo.org/records/10273539](https://zenodo.org/records/10273539) (Zhang, 2023).
Author contributions. XZ Data Curation, Writing - Original Draft, Visualization.

LW, NW, SM and DZ Investigation, Visualization, Data Curation. DZ, HZ and MW Investigation. SW Conceptualization, Data Curation, Supervision. RZ Data Curation, Funding acquisition. All people involve in discussion of the results.

Supplement. The supplement related to this article is available online at: XXX.

Competing interest. The authors declare no competing financial interest.

Financial support. This work was supported by the China Postdoctoral Science Foundation (2023M733220), the Zhengzhou PM$_{2.5}$ and O$_3$ Collaborative Control and Monitoring Project (20220347A) and the National Key Research and Development Program of China (No. 2017YFC0212403).
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