High atmospheric oxidation capacity drives wintertime nitrate pollution in the eastern Yangtze River Delta of China

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Abstract

Nitrate aerosol plays an increasingly important role in wintertime haze pollution in China. Despite intensive research on the wintertime nitrate chemistry in recent years, quantitative constraints on the formation mechanisms of nitrate aerosol in the Yangtze River Delta (YRD), one of the most developed and densely populated regions in eastern China, remain inadequate. In this study, we identify the major nitrate formation pathways and their key controlling factors during the winter haze pollution period in the eastern YRD using two-year (2018-2019) field observations and detailed observation-constrained model simulations. We find that the high atmospheric oxidation capacity, coupled with high aerosol liquid water content (ALWC), made both the heterogeneous hydrolysis of dinitrogen pentoxide (N₂O₅) and the gas-phase OH oxidation of nitrogen dioxide (NO₂) important pathways for wintertime nitrate formation in this region, with contribution percentages of 69% and 29% in urban areas and 63% and 35% in suburban areas, respectively. We further find that the gas-to-particle partitioning of nitric acid (HNO₃) was very efficient so that the rate-determining step in the overall formation process of nitrate aerosol was the oxidation of NOₓ to HNO₃ through both heterogeneous and gas-phase processes. The atmospheric oxidation capacity (i.e., the availability of O₃ and OH radicals) was the key factor controlling the production rate of HNO₃ from both processes. During the COVID-19 lockdown (January-February 2020), the enhanced atmospheric oxidation capacity greatly promoted the oxidation of NOₓ to nitrate and hence weakened the response of nitrate aerosol to the emission reductions in urban areas. Our study sheds light on the detailed formation mechanisms of wintertime nitrate aerosol in the eastern YRD and highlights the demand for the synergetic regulation of atmospheric oxidation capacity and NOₓ emissions to mitigate wintertime nitrate and haze pollution in eastern China.
1. Introduction

Atmospheric fine particulate matter (PM$_{2.5}$) has profound impacts on air quality, climate, and public health (Huang et al., 2014; Wang et al., 2014; Lelieveld et al., 2015; von Schneidemesser et al., 2015). Over the past decades, China has encountered severe PM$_{2.5}$ pollution due to the rapid urbanization and industrialization (Huang et al., 2014; Zhang and Cao, 2015; Tao et al., 2017; Peng et al., 2021). To tackle severe air pollution, Chinese government has implemented active clean air policies such as the “Action Plan for Air Pollution Prevention and Control” in recent years. As a result, anthropogenic emissions of major air pollutants such as sulfur dioxide (SO$_2$), nitrogen oxides (NO$_x$), and primary PM have declined dramatically and the nationwide PM$_{2.5}$ air quality have improved significantly (Shao et al., 2018; Zheng et al., 2018; Ding et al., 2019; Zhang et al., 2019). In addition, with the emission reduction of primary PM, secondary aerosol has become the most important component of PM$_{2.5}$ (Shao et al., 2018; Ding et al., 2019; Peng et al., 2021).

Secondary inorganic aerosol consisting mainly of nitrate, sulfate, and ammonium (SNA), contributed to 30-60% of the PM$_{2.5}$ mass in China (Hua et al., 2015; Tao et al., 2017; Ye et al., 2017; Wang et al., 2018; Fu et al., 2020; Lin et al., 2020). During the pollution episodes, the proportion of SNA to PM$_{2.5}$ could exceed 50% (Tao et al., 2017; Liu et al., 2020; Peng et al., 2021). Before 2013, sulfate was often found to be the most abundant component of PM$_{2.5}$ in Chinese cities (Zhao et al., 2013; Huang et al., 2014; Kong et al., 2014; Xie et al., 2015; Tao et al., 2017). However, with the implementation of stringent clean air policies, anthropogenic emissions of SO$_2$ in China had dropped by 59% from 2013 to 2017, while NO$_x$ emissions decreased only by 21% during the same period (Zheng et al., 2018). Consequently, sulfate aerosol concentration has decreased dramatically nationwide since 2013, but wintertime nitrate concentration has not decreased much (Ding et al., 2019; Li et al., 2019a; Xu et al., 2019; Fu et al., 2020; Wang et al., 2020b); nitrate has become an increasingly important component of PM$_{2.5}$ in most regions of China during winter (Ye et al., 2017; Yun et al., 2018; Li et al., 2019a; Xu et al., 2019; Chen et al., 2020; Fu et al., 2020; Kong et al., 2020; Lin et al., 2020; Xie et al., 2020; Zhai et al., 2021; Zhang et al., 2021). The high loading of nitrate has been considered playing an important role in winter haze pollution (Wen et al., 2015; Sun et al., 2018). Therefore, identifying the major nitrate formation pathways and their controlling factors during haze events is of great importance for developing effective particulate pollution mitigation policies in China.

In polluted regions, the nitrate aerosol arises mainly from two pathways: (1) the gas-phase oxidation of nitrogen dioxide (NO$_2$) by OH radicals producing nitric acid (HNO$_3$) (Calvert and Stockwell, 1983) and (2) the heterogeneous hydrolysis of dinitrogen pentoxide (N$_2$O$_5$) that was produced from the reaction of NO$_2$ with nitrate (NO$_3$) radicals, on aqueous aerosols (Bertram and Thornton, 2009; Bertram et al., 2009; Wagner et al., 2013; McDuffie et al., 2019). The gas-phase OH + NO$_2$ pathway primarily occurs during the daytime and is mainly influenced by the atmospheric oxidation capacity despite the NO$_2$ concentration (Chen et al., 2020; Fu et al., 2020). The heterogeneous formation of nitrate via N$_2$O$_5$ hydrolysis is greatly affected by aerosol liquid water content (ALWC) and the
production of N$_2$O$_5$ (Alexander et al., 2020; Lin et al., 2020; Wang et al., 2020b). As a result, this heterogeneous pathway is generally weak during the daytime because of the fast photolysis of NO$_3$ radicals or titration by NO (Wayne et al., 1991; Brown and Stutz, 2012), which inhibit N$_2$O$_5$ production. However, it could be the dominant pathway for nitrate formation during the nighttime (Wang et al., 2017; McDuffie et al., 2019), where N$_2$O$_5$ can be produced more efficiently and its hydrolysis is favored by the high relative humidity (or ALWC).

There have been a number of field studies on the pollution characteristics and formation mechanisms of nitrate aerosol during haze events in China over the past decades (Tao et al., 2016; Li et al., 2018; Sun et al., 2018; Wen et al., 2018; Ding et al., 2019; Ye et al., 2019; Chen et al., 2020; Fu et al., 2020; Lin et al., 2020; Wang et al., 2020b; Zhao et al., 2020a; Chan et al., 2021). However, most of these studies were carried out in the North China Plain (NCP) (Li et al., 2018; Wen et al., 2018; Chen et al., 2020; Fu et al., 2020; Wang et al., 2020b; Chan et al., 2021). Earlier studies suggested that the nitrate formation during the pollution episodes in this region was mainly attributed to the heterogeneous hydrolysis of N$_2$O$_5$ (Su et al., 2017; Wang et al., 2017; He et al., 2018; Li et al., 2018). However, recent studies showed that the gas-phase OH + NO$_2$ process has become more important, and sometimes this process was even the dominant pathway for nitrate formation (Chen et al., 2020; Fu et al., 2020). The Yangtze River Delta (YRD) in eastern China is one of the most developed regions in China (Ding et al., 2013). The wintertime O$_3$ concentration is relatively high in this region, with an average of ~20 ppb, and sometimes could even reach 75 ppb (Li et al., 2019c; Ye et al., 2019; Zhao et al., 2020a), which is significantly higher than that (average: 6-16 ppb) in the NCP region (Li et al., 2019a; Duan et al., 2020; Liu et al., 2020). Furthermore, the relative humidity (RH) in this region is also high, with the average winter RH ranging from 63% to 71% (Tao et al., 2016; Shen et al., 2020; Yu et al., 2020b), which was also significantly higher than the average RH (20-40%) in the NCP region (Fang et al., 2019; Li et al., 2019a; Huang et al., 2020; Xie et al., 2020). The high atmospheric oxidation capacity, coupled with the high RH that led to high ALWC, would favor the production of secondary aerosol (Peng et al., 2021).

Haze pollution events frequently occurred in the YRD during winter (Hua et al., 2015; Sun et al., 2018; Ding et al., 2019). Although there have been many studies on the pollution characteristics of nitrate and PM$_{2.5}$ in this region (Tao et al., 2016; Sun et al., 2018; Chen et al., 2019; Ding et al., 2019; Ye et al., 2019; Lin et al., 2020; Shen et al., 2020), only a few studies have focused on the nitrate formation mechanisms. It has been reported that the heterogeneous hydrolysis of N$_2$O$_5$ contributed dominantly to nitrate formation in the western YRD (Sun et al., 2018), and its production rate could be 5 times higher than that of the gas-phase OH + NO$_2$ process during severe haze pollution events (Lin et al., 2020). In contrast, some other studies have qualitatively pointed out that the gas-phase OH + NO$_2$ reaction was an important formation pathway of nitrate in the eastern YRD, though the heterogeneous hydrolysis of N$_2$O$_5$ during the nighttime also contributed (Ye et al., 2019; Zhao et al., 2020a). Overall, quantitative constraints on the detailed formation mechanisms of wintertime nitrate aerosol in the YRD region remain limited. The relative
contribution of different nitrate formation pathways and their controlling factors are still unclear. In this study, we conducted hourly measurements of nitrate and associated particulate and gaseous air pollutants at an urban site and a regional site in the eastern YRD during winter in 2018 and 2019, aiming to clarify the nitrate formation mechanisms during winter. An observation-constrained box model using the detailed Master Chemical Mechanism (MCM v3.3.1) updated with the state-of-the-art heterogeneous chemistry of N2O5, NO2, and particulate nitrate was employed to quantitatively identify the major reaction pathways and key controlling factors for wintertime nitrate aerosol formation in this region. This study will help to understand the nitrate aerosol chemistry in the eastern YRD and develop effective strategies to mitigate secondary aerosol pollution in this densely populated region.

2. Materials and methods

2.1 Observation sites and instrumentation

PM2.5 and its chemical composition, inorganic gases, volatile organic compounds (VOCs), and meteorological parameters were continuously measured at a regional site (Qingpu) and an urban site (Pudong) in Shanghai from December 1 to February 12 in both 2018 and 2019. The Qingpu site (120.989 °E, 31.097 °W) is a suburban site (see Fig. 1), located near the Dianshan Lake and surrounded by the residential areas and vegetation, and about 46 km away from the urban Shanghai. Besides, the Qingpu site is located at the junction of Shanghai, Jiangsu, and Zhejiang province and is a typical regional site in the eastern YRD. The instruments at this site were on the rooftop of a 10 m tall building. The Pudong site (121.533 °E, 31.228 °W) is an urban site located near the Century Avenue with heavy traffic, and it is only ~3 km from the business center Lujiazui. The instruments at this site were located on the roof of a 20 m tall building. The eastern YRD region is affected by the subtropical monsoon climate, dominated by the northwest and northeast winds in winter.

The measurements at the two sites were conducted hourly. The PM2.5 mass concentration was measured by a Tapered Element Oscillating Microbalance combined with Filter Dynamic Measurement System (TEOM-FDMS, TEOM 1405-F, Thermo Fisher Scientific, USA.). Water-soluble ions including NO3-, SO4^2-, NH4+, Cl-, Na+, Ca2+, and Mg2+ were measured using an online Monitor for Aerosol and Gases (MARGA, ADI 2080, Applikon Analytical B.B.Corp., Netherlands). Organic carbon (OC) and elemental carbon (EC) were measured by a semi-continuous OC/EC analyzer (Model 4, Sunset Laboratory Inc., USA), and a denuder was installed before analyzer to avoid the disturbance of organic vapors. The surface area and volume concentrations of aerosol particles were measured using a scanning mobility particle sizer (SMPS, TSI, USA, which consists of a 3080 electrostatic classifier, a 3081A different mobility analyzer, and a 3787 condensation particle counter) and an aerodynamic particle sizer (APS 3321, TSI, USA). The combination of SMPS and APS was able to cover the particle size range from 13.6 nm to 10 μm. Considering that the Pudong sampling site lacks the data of aerosol volume and surface area concentrations, we performed a linear fit between the aerosol surface/volume and PM2.5 mass concentration at the...
on such a linear fit and the measured PM$_{2.5}$ mass concentration. The surface/volume concentrations of dry aerosol particles measured by SMPS and APS were corrected to the ambient RH based on an empirical composition-kappa function and the kappa–Köhler function (see details in Section S1 of the Supplement). The O$_3$, NO$_x$, and SO$_2$ were measured by an Ozone, NO$_x$, and SO$_2$ analyzer (Model 49i, 42i, and 43i, Thermo Fisher Scientific, USA), respectively. A total of 56 VOCs were measured using gas chromatography equipped with a flame ionization detector (GC-FID, Chromatotec A11000/A21022 at the Qingpu site and PerkinElmer Clarus 580 at the Pudong site). Meteorological parameters including temperature, RH, pressure, wind speed and direction were measured by a meteorological transducer (WXT520, Vaisala Ltd., Finland).

### 2.2 Estimation of aerosol liquid water content and pH

The ISORROPIA-II thermodynamic model was used to calculate aerosol pH and ALWC (Fountoukis and Nenes, 2007). The water-soluble inorganic ion concentrations, along with RH and temperature, were used as the model input. The model was run in the forward mode, which would give a more accurate estimation of aerosol pH than using the reverse mode with only particulate inorganic ions as the model input (Guo et al., 2015; Hennigan et al., 2015). Besides, considering the relatively high RH in eastern YRD, we selected the metastable state for aerosol in this study. ISORROPIA-II calculated the equilibrium concentrations of particle hydronium ions ($H^+_{aq}$, μg m$^{-3}$) and ALWC (μg m$^{-3}$) in per air volume. Then the aerosol pH can be derived by the following equation:

$$pH = -\log_{10}(H^+_{aq}) = -\log_{10} \frac{1000H^+_{aq}}{ALWC}$$

Where $H^+_{aq}$ is the concentration of hydronium ions in aqueous aerosol (mol L$^{-1}$). It should be mentioned that when the RH was extremely high (> 95%), a slight deviation in measured RH would cause significant uncertainty in the estimation of ALWC. Therefore, we only considered the data with the RH below 95% in the further analysis.

### 2.3 Observation-constrained model simulation

The Framework for 0-D Atmospheric Modeling (F0AM v3.1) (Wolfe et al., 2016) employing the MCM v3.3.1 (Jenkin et al., 2015) was used to simulate the formation of nitrate in the pollution events during the whole observation period. Figure 2 summarizes the formation pathways of HNO$_3$ in the atmosphere (Alexander et al., 2020; Chan et al., 2021). In the model, we considered the reaction pathways including heterogeneous hydrolysis of N$_2$O$_5$ (R3) and NO$_2$ (R8), gas-phase OH + NO$_2$ (R7), NO$_3$ radical oxidation of VOCs (R5), and reaction of NO with hydroperoxy (HO$_2$) radicals (R2), which together contributed to 88% of HNO$_3$ formation in the global troposphere (Alexander et al., 2020). The model did not include the hydrolysis of NO$_3$ radicals and organic nitrate (R1, R4, and R6), as well as the reaction of NO$_2$ with halogen oxide species (R9). However, these pathways only had a small contribution to the production of HNO$_3$ (Alexander et al., 2020). Therefore, they would not significantly affect the model results in this study.
The default MCMv3.3.1 does not consider the heterogeneous hydrolysis of N$_2$O$_5$ in detail and the heterogeneous production of nitrous acid (HONO), an important precursor of OH radicals in the polluted atmosphere. Therefore, we parameterized these processes in the model based on recent advances in these processes. The rate of the heterogeneous hydrolysis of N$_2$O$_5$ on aqueous aerosols ($k_3$) could be calculated by eq. 2 when ignoring the gas-phase diffusion limitation:

$$k_3 = \gamma_{N_2O_5} \cdot c \cdot S_a$$  \hspace{1cm} (2)

where $\gamma_{N_2O_5}$ is the uptake coefficient of N$_2$O$_5$, defined as the probability of removal of N$_2$O$_5$ per collision with the wet aerosol surface; $c$ is the mean molecular speed of N$_2$O$_5$; $S_a$ is the measured aerosol surface area concentration. In this study, we employed an observation-based empirical parameterization of $\gamma_{N_2O_5}$, which provided a reasonable representation of the PM$_{2.5}$ reactivity toward N$_2$O$_5$ at different Chinese sites, according to a recent study (Yu et al., 2020a):

$$\gamma_{N_2O_5} = \frac{4}{c} \frac{V_a}{S_a} K_H \times 3.0 \times 10^{-4} \times [H_2O] \times \left(1+\frac{1}{0.033 \times [H_2O]_{NO_3^-} + 3.4 \times [Cl^-]_{NO_3^-}}\right)$$  \hspace{1cm} (3)

where $V_a$ is the measured aerosol volume concentration; $K_H$ is the Henry’s law coefficient of N$_2$O$_5$, with a value of 51 M atm$^{-1}$ (Bertram and Thornton, 2009); and [H$_2$O], [NO$_3^-$], and [Cl$^-$] are the molarity of water, nitrate, and chloride in aerosol, respectively.

The heterogeneous hydrolysis of N$_2$O$_5$ on aqueous aerosols could form HNO$_3$ and/or nitryl chloride (CINO$_2$) (see R3), with their yields (i.e., the value of $\Phi$, ranging between 0 and 1) depending on the H$_2$O and Cl$^-$ content in the aerosol (Bertram and Thornton, 2009; Yu et al., 2020a). In this study, the yield of HNO$_3$ ($\Phi_{HNO_3}$) was estimated from eq. 4 (Bertram and Thornton, 2009; Yu et al., 2020a):

$$N_2O_5 + Aerosol \rightarrow 2\Phi HNO_3 + 2(1-\Phi) ClNO_2$$  \hspace{1cm} (R3)

$$\Phi_{HNO_3} = 1.1/\left(1+\frac{[H_2O]}{105 \times [Cl^-]}\right)$$  \hspace{1cm} (4)

Photolysis of HONO was shown to contribute 20-92% of the production of OH radicals during winter haze pollution events in China (Tan et al., 2017; Slater et al., 2020; Xue et al., 2020). Here, on the basis of previous studies (Lee and Schwartz, 1983; Kleffmann et al., 1998; Kurtenbach et al., 2001; Wong et al., 2011; Wong et al., 2013; Han et al., 2016; Ye et al., 2016; Liu et al., 2017; Trinh et al., 2017; Romer et al., 2018; Zare et al., 2018; Liu et al., 2019; Wang et al., 2020a; Xue et al., 2020), we parameterized the major heterogeneous production pathways of HONO and its dry deposition to estimate the HONO budget during the pollution episodes. The added mechanisms are summarized in Table 1. A detailed description of the parameterization is provided in the Supplement (Section S2). Considering that there remain significant uncertainties in the key parameters (i.e., the uptake coefficient of NO$_2$ on aerosol or ground surfaces, EF, and HONO emission ratios) of the heterogeneous HONO formation pathways and its direct emissions as listed in Table 1, we performed the sensitivity analyses for these parameters to evaluate their influences on the model.
In addition, we included the dry deposition of HNO₃ with a velocity (vHNO₃) of 0.0175 m s⁻¹ (Liu et al., 2019). The rate constant of the deposition was then calculated using eq. 5:

\[ k_{dep} = \frac{v_{HNO_3}}{PBL} \]  

where PBL is the planetary boundary layer height. We also considered the dilution of all other species via deposition, entrainment, etc. using a highly simplified parameterization:

\[ \frac{d[X]}{dt} = -k_{dil}(X - X_{bkg}) \]  

where \( k_{dil} \) is the first-order dilution rate constant; \( X_{bkg} \) is a fixed background concentration of pollutants. Here, a typical dilution lifetime of one day was assumed, i.e., \( k_{dil} = 1/86400 \) s⁻¹. As the species background concentration was unknown, \( X_{bkg} \) was set to 0 for simplicity.

In the model, the \( j \) values of various gaseous species were calculated using the default MCMv3.3.1 parameterization with input of the solar zenith angle at the observations sites and scaled by the ratio of measured to calculated \( jNO_2 \) values. The observed pollutant concentrations and meteorological parameters were used as the model input, which were updated hourly (one model step) using the observation data and held constant during each model step, except for the observed concentrations of NO and NO₂ (the sum of NO and NO₂ concentrations was also constrained by the observation).

3. Results and Discussion

3.1 Overview of pollution characteristics during winter

Table 2 shows the overall pollution conditions of the two observation sites in winter 2018 and 2019. The average PM₂.₅ concentration increased by 17-21% in 2019 compared to that in 2018. Accordingly, nitrate concentration also increased by 11-14% in 2019. The \( O_3 \) concentration was slightly higher in 2019 than in 2018, consistent with increased atmospheric oxidation capacity in recent years (Lu et al., 2018; Li et al., 2019b; Liu and Wang, 2020; Yang et al., 2020). In the two years, both of the PM₂.₅ and nitrate concentrations at the Qingpu site were higher than those at the Pudong site. As mentioned above, the Qingpu site is at the junction of Shanghai, Jiangsu, and Zhejiang, so it is more easily influenced by the transport of air pollutants from Jiangsu, which is usually more polluted than Shanghai. Besides, the average temperature at the Qingpu site was also slightly lower than that at the Pudong site, which might to some extent favor the gas-to-particle partitioning of HNO₃. Notably, the average RH was as high as 80% during the observation period, which was significantly higher than that (63%) recorded in 2016 (Tao et al., 2016). In particular, the RH exceeded 90% for more than one third of the days during the observation period.

Taking the Pudong site in 2019 as an example, we analyzed the time series of PM₂.₅, nitrate, and other related parameters and presented the results in Figure 3 (Time series of the pollutants at the Qingpu site can be seen in Section S3 and Figure S2). PM₂.₅ pollution events occurred frequently in
During the observation period, the PM$_{2.5}$ concentration exceeded 75 µg m$^{-3}$ for 34 days and 150 µg m$^{-3}$ for 6 days. During the pollution episodes (PM$_{2.5}$ > 75 µg m$^{-3}$), nitrate had become the most important component of PM$_{2.5}$, and its concentration was a factor of 2.2 higher than that of sulfate. In winter, the emission of NO$_x$ was obviously high. During the periods with high nitrate concentration, the NO$_x$ concentration always exceeded 100 ppb. The O$_3$ concentration was also at a relatively high level, with a maximum value of 60 ppb and an average of 22 ppb, which was much higher than the wintertime average O$_3$ concentration (6-16 ppb) in the NCP (Li et al., 2019a; Duan et al., 2020; Liu et al., 2020). The concentration of odd oxygen (O$_x$=O$_3$+NO$_2$) ranged between 20-83 ppb with an average of 44 ppb, indicating a relatively high atmospheric oxidation capacity in the eastern YRD during winter. Consistently, the nitrogen oxidation ratio (NOR, NOR = NO$_3$/(NO$_3$ + NO$_2$)) was up to 0.51, suggesting a high degree of atmospheric oxidation. Meanwhile, the high atmospheric RH in the eastern YRD led to a high ALWC. During the high nitrate periods, the ALWC was often at its peak and could exceed 200 µg m$^{-3}$ on rainy or haze-foggy days. Such a high ALWC level would have an important impact on the nitrate formation. Notably, the NO$_x$ concentration dropped sharply on 23 January and kept at a low level until the end of the observation (12 February, 2020). This is mainly a result of marked emission reductions during the COVID-19 lockdown. Such an emission reduction had a complicated influence on the nitrate formation chemistry, which will be discussed in detail in Section 3.5.

Figure 4 shows the mass ratio of nitrate to PM$_{2.5}$ as a function of the PM$_{2.5}$ concentration and ALWC at Qingpu and Pudong sites in 2018 and 2019. The ratio of nitrate to PM$_{2.5}$ increased with increasing PM$_{2.5}$ concentration. When the PM$_{2.5}$ concentration was above 75 µg m$^{-3}$, the average mass fraction of nitrate was more than 30%. In addition, the nitrate formation rate was much higher than that of sulfate and ammonium during PM$_{2.5}$ pollution episodes, as indicated by the slope of nitrate vs. PM$_{2.5}$ that was twice that of the other two ions (see Figure S3). These results indicate that the formation of nitrate played a driving role in the formation of PM$_{2.5}$ pollution. In general, when the ALWC was high, the nitrate concentration was also at a high level. On one hand, ALWC could promote the nitrate formation by favoring the heterogeneous hydrolysis of N$_2$O$_5$ and the gas-to-particle partitioning of HNO$_3$. On the other hand, the increase in nitrate concentration could enhance the hygroscopicity of PM$_{2.5}$, leading to an increase in ALWC, which would further promote the nitrate formation (Wang et al., 2020b). It is worth noting that, when PM$_{2.5}$ < 100 µg m$^{-3}$, the mass ratio of NO$_3$ to PM$_{2.5}$ increased rapidly with rising PM$_{2.5}$ concentration, but when the PM$_{2.5}$ concentration exceeded 100 µg m$^{-3}$, the ratio reached a plateau. This might be due to the fact that when the PM$_{2.5}$ concentration increased to a certain level, the formation process of other components may also speed up, causing the nitrate proportion to stay basically constant.

### 3.2 Gas-to-particle partitioning of nitrate

The gas-to-particle partitioning of nitrate determines the sensitivity of particulate nitrate formation to the production of HNO$_3$. Figure 5 shows the particulate nitrate concentration (measured) and its fraction to total nitrate (εHNO$_3$, εHNO$_3$ = NO$_3$/(NO$_3$+HNO$_3$), predicted by ISORROPIA-II) as a
function of ALWC and aerosol pH. In order to avoid the influence of rainy and foggy days during the observation period which could lead to the abnormal high ALWC, we only used the data with RH below 95% for analysis. Obviously, ALWC promoted the formation of particulate nitrate, but such a promoting effect varied greatly under different aerosol pH (top panel in Figures 5a-d). As the pH increased, the slope of nitrate vs. ALWC also increased significantly, indicating a stronger promoting effect. ALWC plays a dual role in the formation of nitrate aerosol: it can promote the heterogeneous formation of nitrate, e.g., via N$_2$O$_5$ hydrolysis, by providing more reaction medium and decreasing the kinetic limitation (Mozurkewich and Calvert, 1988; Bertram and Thornton, 2009; Wang et al., 2020b); the ALWC can also promote the gas-to-particle partitioning of HNO$_3$. The different promoting effect of ALWC under different aerosol pH is mainly due to the fact that pH can significantly influence the gas-to-particle partitioning of HNO$_3$. As shown in Figures 5a-d (bottom panel), when the aerosol pH was low, the gas-to-particle partitioning of HNO$_3$ was inhibited, with the value of $\epsilon_{\text{HNO}_3}$ basically below 0.6 at pH < 2. Under these conditions, the increase of particulate nitrate concentration would require more ALWC. When the pH increased, the inhibition effect of pH on the gas-to-particle partitioning of HNO$_3$ was weakened. When the pH was higher than 2.5, the nitrate was almost in the particle phase ($\epsilon_{\text{HNO}_3}$=1). As a result, the increase of ALWC would rapidly promote the nitrate formation, particularly when ALWC was at a low level. It is important to point out that during the whole observation period, the values of $\epsilon_{\text{HNO}_3}$ were larger than 0.9 for 90% of time when the PM$_{2.5}$ concentration was higher than 75 $\mu$g $\text{m}^{-3}$ (see Figure S4). This indicates that the gas-to-particle partitioning of HNO$_3$ was very efficient and not a limiting factor for particulate nitrate formation during the pollution episodes. The gas-to-particle partitioning of HNO$_3$ was also efficient in the NCP region, and its average $\epsilon_{\text{HNO}_3}$ could reach 100% during the haze pollution period (Guo et al., 2018; Li et al., 2019a). However, the average $\epsilon_{\text{HNO}_3}$ in the northeastern United States during winter was only 39% (Guo et al., 2018), this might be due to the relatively lower pH in this region (0.8 ± 1.0) (Guo et al., 2016), which inhibited the gas-to-particle partitioning.

### 3.3 Observational constraints on the nitrate formation mechanism

The nitrate formation mechanism is different during the different time of a day. The heterogeneous hydrolysis of N$_2$O$_5$ was often found to be an important pathway for nighttime nitrate formation. Here, we evaluated the role of this pathway to nitrate formation in the eastern YRD using the correlation between particulate nitrate concentration and the production of N$_2$O$_5$ during nighttime. Due to the lack of direct observational data of N$_2$O$_5$ in this study, we used the value of square of NO$_2$ multiplied by O$_3$ ([NO$_2$]$^2$×O$_3$) to indicate the N$_2$O$_5$ level (Liu et al., 2020). Figure 6 shows the nitrate concentration as a function of [NO$_2$]$^2$×O$_3$ during the nighttime in winter. The particulate nitrate concentration showed a strong positive correlation with [NO$_2$]$^2$×O$_3$. In particular in 2018, as the value of [NO$_2$]$^2$×O$_3$ increased to 15000, the nitrate concentration increased from 5-10 $\mu$g $\text{m}^{-3}$ to 25-30 $\mu$g $\text{m}^{-3}$, suggesting that the heterogeneous hydrolysis of N$_2$O$_5$ was an important pathway for wintertime nitrate formation in the eastern YRD. Notably, there are some data points with low values of [NO$_2$]$^2$×O$_3$ but high nitrate concentrations. This might be partly due to their relatively high aerosol pH (> 3), which could promote the gas-to-particle partitioning of HNO$_3$. 

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To evaluate the role of the gas-phase OH + NO$_2$ process in nitrate formation during the daytime, we use the Ox to indicate the atmospheric oxidation capacity due to the lack of direct observational data of OH radicals. Figure 7 shows the particulate nitrate concentration as a function of Ox during the daytime. Notably, as the Ox concentration increased, the nitrate concentration also increased significantly. However, the increase in ALWC seemed to have a relatively small impact on the nitrate concentration during the daytime, indicating that the reaction of NO$_2$ with OH radicals to form HNO$_3$ (rather than the gas-to-particle partitioning) was a rate-limiting step in daytime nitrate formation. We also note that there are some data points with low Ox values but high ALWC and nitrate concentrations (Figure 7c). This phenomenon might be owing to a certain degree of heterogeneous process in the haze-foggy days, when the photochemical reactions were relatively weaker. Overall, the high atmospheric oxidation capacity made the gas-phase OH + NO$_2$ reaction an important pathway for nitrate formation during the daytime in the eastern YRD.

3.4 Model constraints on the nitrate formation mechanism

To quantify the contribution of different formation mechanisms to wintertime nitrate formation in the eastern YRD, we used an observation-constrained model (FOAM v3.1) updated with the heterogeneous chemistry of N$_2$O$_5$ and NO$_2$ (see Section 2.3 for details) to simulate the formation rate of HNO$_3$ from different pathways during the observation period. During the winter of 2019, six haze pollution episodes (PM$_{2.5} > 75$ μg m$^{-3}$) occurred at both sites (there was an additional episode during the outbreak of COVID-19 epidemic, which was discussed separately in Section 3.5). We conducted simulations for all the six pollution episodes and took two representative ones at the Pudong site for the detailed analysis. Considering the large uncertainties in ALWC estimation and aerosol surface area/volume correction at high RH levels (> 95%), which could significantly affect the simulation results, we excluded the simulated data above 95% RH from the further analysis. Figure 8 shows the time series of various particulate (measured) and gaseous (measured and simulated) air pollutants, as well as the formation rate of HNO$_3$ (simulated) from different pathways during these two episodes (The case studies of the same episodes at the Qingpu site are given in Section S4 and Figure S5).

In episode 1 (Figure 8a), the nitrate concentration increased rapidly from 15.2 μg m$^{-3}$ at 22:00 on 29 December to 39.0 μg m$^{-3}$ at 10:00 on 30 December, with an average growth rate of 2.0 μg m$^{-3}$ h$^{-1}$. The simulated NO$_2$ concentration was in good agreement with the observation, except for a short period around the midnight of 30 December, during which the NO emissions led to an over-prediction of the NO$_2$ level. During the high nitrate periods, the nighttime N$_2$O$_5$ concentration could reach 0.5-1 ppb and contributed noticeably to HNO$_3$ formation via the heterogeneous hydrolysis. However, the high daytime OH concentration (up to 2.5 × 10$^6$ molecules cm$^{-3}$) facilitated a relatively more rapid nitrate formation from the gas-phase OH + NO$_2$ pathway. The average production rate of HNO$_3$ from the gas-phase OH + NO$_2$ reaction during the daytime was 2.9 μg m$^{-3}$ h$^{-1}$, which was twice the average production rate of HNO$_3$ from the heterogeneous hydrolysis of N$_2$O$_5$ during the nighttime.
We note that the overestimation of NO\textsubscript{2} during the night of 30 December (case 1) could lead to an overestimation of nighttime HONO, but it did not significantly affect the overall production rate of HONO and thereby OH radicals in this case, which was dominated by the daytime heterogeneous photochemical processes (see Figure S7, HONO production rate in the base scenario). In addition, as the O\textsubscript{3} concentration in the model was constrained by the measured value, which was very low (< 5 ppb) during this time, the overestimation of NO\textsubscript{2} would also not significantly affect the prediction of N\textsubscript{2}O\textsubscript{5}. As a result, the over-prediction of NO\textsubscript{2} would not have a large influence on the major formation pathways of nitrate.

There were two cases in the episode 2 (Figure 8b). In case 2, the concentration of nitrate increased from 26.8 \(\mu\text{g m}^{-3}\) at 05:00 to 46.0 \(\mu\text{g m}^{-3}\) at 13:00 on 12 January, 2020, with an average growth rate of 2.4 \(\mu\text{g m}^{-3}\) h\textsuperscript{-1}. Then, the nitrate concentration achieved a fast growth from 40.2 to 70.5 \(\mu\text{g m}^{-3}\) within only six hours during the night of 12 January, with an average rate of 5.1 \(\mu\text{g m}^{-3}\) h\textsuperscript{-1}. During the nitrate increasing period, the maximum OH concentration was \(\sim 1.0 \times 10^6\) molecules cm\textsuperscript{-3}. As a result, the gas-phase OH + NO\textsubscript{2} reaction led to a slow increase of nitrate concentration in the daytime of 12 January. During the nighttime, the N\textsubscript{2}O\textsubscript{5} concentration quickly increased to 0.83 ppb. The high N\textsubscript{2}O\textsubscript{5} level, in combination with the high ALWC, made the heterogeneous hydrolysis of N\textsubscript{2}O\textsubscript{5} a more important pathway for nitrate formation. The simulated average production rate of HNO\textsubscript{3} from the heterogeneous hydrolysis of N\textsubscript{2}O\textsubscript{5} during this case was 4.0 \(\mu\text{g m}^{-3}\) h\textsuperscript{-1}, which was 3.6 times that of the formation rate from the gas-phase OH + NO\textsubscript{2} reaction (1.1 \(\mu\text{g m}^{-3}\) h\textsuperscript{-1}). In case 3, the nitrate concentration increased from 22.5 \(\mu\text{g m}^{-3}\) at 00:00 to 53.8 \(\mu\text{g m}^{-3}\) at 11:00 on 14 January, with an average growth rate of 2.8 \(\mu\text{g m}^{-3}\) h\textsuperscript{-1}. The N\textsubscript{2}O\textsubscript{5} concentration was at a high level (~ 1 ppb) during the nighttime and its hydrolysis contributed significantly to nitrate formation at the beginning of the nitrate-increasing period. In the morning of 14 January, the OH concentration rapidly increased to \(1.3 \times 10^6\) molecules cm\textsuperscript{-3}, resulting in considerable nitrate formation from the gas-phase process. The average production rates of HNO\textsubscript{3} from the heterogeneous and gas-phase processes in this case were 3.9 and 2.4 \(\mu\text{g m}^{-3}\) h\textsuperscript{-1}, respectively, suggesting that both processes were important nitrate formation pathways.

As mentioned above, there were six haze pollution episodes during the observation period. At the Qingpu site, the heterogeneous hydrolysis of N\textsubscript{2}O\textsubscript{5} was the major formation pathway (65-80%) of nitrate aerosol for four episodes, while the gas-phase OH + NO\textsubscript{2} reaction had a major contribution (54-60%) for the other two episodes. At the Pudong site, the heterogeneous process also contributed dominantly (67-89%) to nitrate formation during four episodes, and for the other two episodes, the contributions of the heterogeneous and gas-phase processes were comparable (51-53% vs. 45-47%). Figure S6 shows the average diurnal variation of the production rates of HNO\textsubscript{3} from different pathways during the observation period in 2019. The gas-phase process produced HNO\textsubscript{3} mainly from 7:00 to 16:00, while the HNO\textsubscript{3} production from the heterogeneous process occurred mainly from 17:00 to 6:00. The average production rates of HNO\textsubscript{3} from the heterogeneous and gas-phase
processes are given in Figure 9. At the Qingpu site, the average production rate of HNO₃ from the two processes was 3.79 μg m⁻³ h⁻¹ for the heterogeneous process during the nighttime (14 hours) vs. 2.94 μg m⁻³ h⁻¹ for the gas-phase reaction during the daytime (10 hours). The production rate from other processes such as NO₂ hydrolysis and NO₃ radical oxidation of VOCs was only 0.08 μg m⁻³ h⁻¹. Therefore, the heterogeneous and gas-phase processes contributed to 63% and 35% of nitrate formation at this site, respectively. At the Pudong site, the average formation rate of HNO₃ from the hydrolysis of N₂O₅ was 3.83 μg m⁻³ h⁻¹, significantly higher than that from the gas-phase reaction (2.27 μg m⁻³ h⁻¹). As a result, the contributions of heterogeneous and gas-phase processes to nitrate formation were 69% and 29%, respectively.

It should be noted that significant uncertainties remain in the key parameters of the heterogeneous HONO formation pathways in the model, which could affect the prediction of the OH level and thereby gas-phase formation of HNO₃. However, sensitive analyses for various parameters show that the current parameterization of these heterogeneous reactions in the model (see Table 1) allows for robust quantitative constraints on the relative contributions of the gas-phase and heterogeneous processes to nitrate formation during haze pollution episodes (see Section S5 and Figure S7 for more details).

As discussed in Section 3.2, the gas-to-particle partitioning of HNO₃ was rather efficient, with the value of ε_HNO₃ larger than 0.9 for 90% of the time during the haze pollution periods. Therefore, the overall formation rate of particulate nitrate would be determined by the production rate of HNO₃ from the heterogeneous hydrolysis of N₂O₅ and gas-phase OH + NO₂ reaction. To identify the key chemical factors that controlled the production rates of HNO₃ from these two major reaction pathways, the relationships between the HNO₃ production rate and concentrations of NO₂ and oxidants (i.e., O₃ or OH radicals) are examined and plotted in Figure 10.

As shown in Figure 10a, the slopes of the HNO₃ production rate from the heterogeneous process vs. NO₂ during the nighttime were different under different O₃ concentrations. When O₃ concentrations were higher than 10 ppb, the increase in NO₂ led to a significant increase in HNO₃ production, with the production rate exceeding 5 μg m⁻³ h⁻¹ when the NO₂ was higher than 30 ppb. However, when the O₃ level was low (< 10 ppb), the heterogeneous process was relatively slow, even with NO₂ concentration exceeding 60 ppb. These results suggest that the atmospheric oxidation capacity (or the availability of O₃), which affected the production of N₂O₅, played a vital role in controlling the nitrate formation rate from the heterogeneous process. Furthermore, the reactive uptake of N₂O₅ by aerosols was found to be very efficient (see Figure S8) so that it was not the rate-limiting step of the heterogeneous nitrate formation during the haze pollution periods. Similarly, the slope of the HNO₃ production rate from the gas-phase process vs. NO₂ during the daytime also varied dramatically under different OH radical concentrations (Figure 10b). As the OH radical concentration was higher than 7 × 10⁵ molecules cm⁻³, this rate increased markedly with the increase in NO₂. This phenomenon proved again that the atmospheric oxidation capacity played a driving role in the...
production of HNO₃ from the gas-phase process.

The results in Figure 10 also suggest that solely reducing the NOₓ emissions might result in an increase of O₃ and OH concentrations, which could enhance the oxidation of NOₓ and thereby offset the effect of NOₓ emission reductions on HNO₃ production. Therefore, a synergistic control of atmospheric oxidant and NOₓ emissions would be of great importance for mitigating wintertime particulate nitrate pollution in the eastern YRD.

3.5 Nitrate aerosol formation during the COVID-19

The city lockdowns during the COVID-19 epidemic resulted in substantial emission reductions from vehicular and industrial sources, which provided an opportunity to investigate the response of secondary aerosols to primary emission reductions. Here, we selected the 23 January, 2019 as a demarcation point (since then many cities in China started to implement lockdown measures) and analyzed the characteristics of particulate nitrate pollution before and during the COVID-19 epidemic.

Figure 11 shows the concentrations of major gaseous and particulate air pollutants, NOR, and sulfur oxidation ratio (SOR) in the eastern YRD before (1-22 January, 2020) and during (23 January-12 February, 2020) the COVID-19 epidemic. At the Pudong site (Figure 11 a, b, c), the average NOₓ concentration decreased by 57% due to marked reductions in vehicular emissions during the epidemic. In contrast, the SO₂ concentration only had a small decrease (16%) during the epidemic, since it mainly comes from coal-combustion sources and is less affected by vehicular emissions. However, the O₃ concentration increased by 66% during the epidemic. This is mainly due to the significant reduction in NOₓ emissions, though the changes in meteorological conditions could also contribute (Zhao et al., 2020b). Accordingly, the model simulations show that the atmospheric OH concentration (median) increased by 14% during the epidemic, though the average value only increased slightly. The increase in O₃ and OH concentrations could significantly promote the oxidation of NOₓ to nitrate and SO₂ to sulfate through both gas-phase and heterogeneous processes.

As shown in Figure 11c, the average values of NOR and SOR increased from 0.15 and 0.46 before the epidemic to 0.21 and 0.50 during the epidemic, respectively. The enhanced oxidation of NOₓ and SO₂ would weaken the response of particulate nitrate and sulfate to the emission reductions. As can be seen in Figure 11b and c, the simulated HNO₃ production rate and measured particulate nitrate concentration dropped by 42% and 40% during the epidemic, respectively, which were both significantly smaller than the decrease in NOₓ concentration (57%), while the particulate sulfate concentration only decreased by 2%, also substantially smaller than the reduction in SO₂ concentration (16%).

Similarly, at the Qingpu site, the NOₓ concentration decreased by 58% during the epidemic, while the concentrations of O₃ and OH radicals (median) increased by 90% and 17%, respectively. The significantly enhanced atmospheric oxidation capacity made the simulated HNO₃ production rate
only decrease by 17% during the epidemic. However, the measured particulate nitrate concentration at this site decreased by 60%, comparable to the decrease in NOx concentration. The inconsistency between the decrease in measured nitrate concentration and simulated HNO3 production rate at the Qingpu site was different from the situation observed at the Pudong site, which is likely due to the fact that the Qingpu site was more easily to be influenced by the regional transport. We note that the average wind speed at the Qingpu site (1.8 m s\(^{-1}\)) was higher than that at the Pudong site (1.1 m s\(^{-1}\)). Besides, the haze pollution was more serious at the Qingpu site than at the Pudong site before the epidemic: both PM\(_{2.5}\) and nitrate concentrations were significantly higher at the Qingpu site (see Figure 11). Therefore, the marked emission reductions on a regional scale during the epidemic would decrease both the local formation and transport of particulate nitrate from the upwind regions, resulting in a more pronounced reduction in observed nitrate concentration at the Qingpu site. In addition, as air plume influenced by the regional transport was more aged, the NOR and SOR values before the epidemic were even higher than those during the epidemic.

The results at the Pudong site clearly show that the enhanced atmospheric oxidation capacity during the COVID-19 epidemic promoted the formation of secondary aerosols and offset the effects of primary emission reductions in the eastern YRD. Such a phenomenon has also been observed in many other regions in China during the COVID-19 lockdown (Le et al., 2020; Zheng et al., 2020; Huang et al., 2021; Liu et al., 2021; Tian et al., 2021; Zhong et al., 2021). These results suggest an important role of atmospheric oxidation capacity in regulating secondary aerosol formation. They also highlight the importance of the synergetic regulation of atmospheric oxidants and other air pollutants in the mitigation of particulate pollution in China. However, the Qingpu site also provided us a special case that in severely polluted regions with a stronger influence from the regional transport, the offset effects of enhanced atmospheric oxidation capacity on emission reductions could be more complicated and less significant.

4. Conclusions

In this study, the chemical mechanisms and key controlling factors of wintertime nitrate formation in the eastern YRD of China were investigated using a combination of online field observations and detailed model simulations. During the observation period (Winter 2018 and 2019), the haze pollution events (PM\(_{2.5}\) > 75 \(\mu\)g m\(^{-3}\)) occurred frequently in this region. The mass fraction of nitrate in PM\(_{2.5}\) increased dramatically with PM\(_{2.5}\) concentration and exceeded 30% throughout the pollution periods. The measured nitrate concentration was well correlated with \([\text{NO}_2]^2\times[\text{O}_3]\) (an indicator of \(\text{N}_2\text{O}_5\)) at night and the level of \(\text{O}_x\) (an indicator of atmospheric oxidation capacity) during the daytime, indicating that both the heterogeneous hydrolysis of \(\text{N}_2\text{O}_5\) and gas-phase OH + \(\text{NO}_2\) process played important roles in wintertime nitrate formation in the eastern YRD.

Observation-constrained model simulations further show that the average production rates of HNO3 from the heterogeneous hydrolysis of \(\text{N}_2\text{O}_5\) during the nighttime and gas-phase OH + \(\text{NO}_2\) reaction during the daytime were 3.81 \(\mu\)g m\(^{-3}\) h\(^{-1}\) and 2.61 \(\mu\)g m\(^{-3}\) h\(^{-1}\), respectively, during the haze pollution periods; these two pathways accounted for 66% and 32% of wintertime nitrate formation in the
eastern YRD, respectively.

The ALWC significantly promoted the formation of nitrate by facilitating the hydrolysis of \( \text{N}_2\text{O}_5 \) and the gas-to-particle partitioning of \( \text{HNO}_3 \). However, the promoting effect of ALWC on nitrate formation varied with aerosol pH due to its significant influence on the gas-to-particle partitioning of \( \text{HNO}_3 \). During the pollution periods, the gas-to-particle partitioning of \( \text{HNO}_3 \) was very efficient, with the partitioning coefficients, \( \varepsilon_{\text{HNO}_3} \), larger than 0.9 for 90% of the time. Therefore, the overall formation processes of wintertime particulate nitrate were not limited by the gas-to-particle partitioning of \( \text{HNO}_3 \) but rather by its production from both heterogeneous and gas-phase processes. Further analyses of the response of \( \text{HNO}_3 \) formation to the variation in the concentrations of \( \text{NO}_2 \), \( \text{O}_3 \), and \( \text{OH} \) radicals suggests that the atmospheric oxidation capacity (i.e., the availability of \( \text{O}_3 \) and \( \text{OH} \) radicals) played a key role in controlling the formation of nitrate from both processes.

During the COVID-19 lockdown (January-February 2020), the enhanced atmospheric oxidation capacity promoted the oxidation of \( \text{NO}_x \) to nitrate and weaken the effects of primary emission reductions on particulate pollution in typical urban areas in the eastern YRD, though such an offset effect was less significant in regions with a stronger influence from the regional transport. This phenomenon again suggests that the atmospheric oxidation capacity played an important role in driving the formation of secondary aerosols, and highlights the importance of the synergetic regulation of atmospheric oxidation capacity and other air pollutants in the mitigation of particulate pollution in eastern China.

Data availability. The data presented in this work are available upon request from the corresponding authors.

Author contributions. YZ designed the study, JH, QZ, QF, and YD performed field measurements, JYS conducted ISORROPIA-II model calculation, JA and CH provided the \( \text{NO}_x \) emission inventory, and YZ and HZ analyzed the data, conducted model simulations, and wrote the paper. All other authors contributed to discussion and writing.

Competing interests. The authors declare no conflict of interest.

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### Table 1 Parameterization of the formation and removal pathways of HONO added to the model.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Parametrization</th>
<th>Max</th>
<th>Min</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NO}_2\text{+aerosol} \rightarrow 0.5\text{HONO}+0.5\text{HNO}_3)</td>
<td>(\gamma_{\text{NO}_2}=2\times10^{-6})</td>
<td>(1\times10^{-5})</td>
<td>(4\times10^{-7})</td>
<td>a-d</td>
</tr>
<tr>
<td>(\text{NO}_2\text{+ground} \rightarrow \text{HONO})</td>
<td>(\gamma_{\text{NO}_2}=2\times10^{-6})</td>
<td>(1\times10^{-5})</td>
<td>(4\times10^{-7})</td>
<td>a-d</td>
</tr>
<tr>
<td>(\text{NO}_2\text{+aerosol+hv} \rightarrow \text{HONO})</td>
<td>(\gamma_{\text{NO}<em>2}=2\times10^{-5} \times \frac{j</em>{\text{NO}<em>2}}{j</em>{\text{NO}_2,\text{noon}}})</td>
<td>(1\times10^{-4})</td>
<td>(4\times10^{-6})</td>
<td>b, e-g</td>
</tr>
<tr>
<td>(\text{NO}_2\text{+ground+hv} \rightarrow \text{HONO})</td>
<td>(\gamma_{\text{NO}<em>2}=2\times10^{-5} \times \frac{j</em>{\text{NO}<em>2}}{j</em>{\text{NO}_2,\text{noon}}})</td>
<td>(1\times10^{-4})</td>
<td>(4\times10^{-6})</td>
<td>b, e-g</td>
</tr>
<tr>
<td>(\text{pNO}_3^-\text{+hv} \rightarrow \text{HONO})</td>
<td>(j_{\text{NO}<em>3^-}=j</em>{\text{HNO}_3}\times30)</td>
<td>100</td>
<td>1</td>
<td>h, i</td>
</tr>
<tr>
<td>Vehicular emission</td>
<td>(\text{HONO/NO}_x=0.8%)</td>
<td>0.18%</td>
<td>1.6%</td>
<td>j-l</td>
</tr>
<tr>
<td>(\text{NO}_2\text{+SO}_2\text{+aerosol} \rightarrow \text{HONO}+\text{SO}_4^2-)</td>
<td>(k_{\text{aq}}=1.4\times10^5\text{ M}^{-1}\text{s}^{-1}) (pH &lt; 5); (2\times10^6\text{ M}^{-1}\text{s}^{-1}) (pH &gt; 6)</td>
<td>m, n</td>
<td></td>
<td></td>
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<tr>
<td>HONO deposition</td>
<td>(k_{\text{dep}}=\exp\left(\frac{23920}{T-91.5}\right)\text{PBL})</td>
<td>a</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The value of \(j_{\text{NO}_2,\text{noon}}\) used in the model was 0.005 s\(^{-1}\); References: \(^a\)Xue et al. (2020); \(^b\)Liu et al. (2019); \(^c\)Wong et al. (2011); \(^d\)Kleffmann et al. (1998); \(^e\)Wong et al. (2013); \(^f\)Zare et al. (2018); \(^g\)Han et al. (2016); \(^h\)Romer et al. (2018); \(^i\)Ye et al. (2016); \(^j\)Kurtenbach et al. (2001); \(^k\)Liu et al. (2017), \(^l\)Trinh et al. (2017); \(^m\)Lee and Schwartz (1983); \(^n\)Wang et al. (2020a).*

### Table 2 Concentrations (average ± standard deviation) of PM\(_{2.5}\), particulate nitrate, NO\(_x\), and O\(_3\), as well as temperature and RH at Qingpu and Pudong sites in the winter of 2018 and 2019.

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>PM(_{2.5}) ((\mu g\text{ m}^{-3}))</td>
<td>50.0 ± 34.8</td>
<td>40.9 ± 32.5</td>
<td>58.6 ± 37.2</td>
<td>49.5 ± 35.3</td>
</tr>
<tr>
<td>NO(_x) ((\mu g\text{ m}^{-3}))</td>
<td>14.9 ± 12.8</td>
<td>11.9 ± 12.2</td>
<td>17.0 ± 14.8</td>
<td>13.2 ± 12.0</td>
</tr>
<tr>
<td>NO(_3^-) (ppb)</td>
<td>29.6 ± 31.1</td>
<td>27.5 ± 24.4</td>
<td>35.1 ± 33.1</td>
<td>26.9 ± 21.3</td>
</tr>
<tr>
<td>O(_3) (ppb)</td>
<td>19.1 ± 12.7</td>
<td>18.8 ± 10.4</td>
<td>21.7 ± 14.3</td>
<td>22.3 ± 12.0</td>
</tr>
<tr>
<td>Temperature ((^\circ\text{C}))</td>
<td>6.6 ± 4.4</td>
<td>7.3 ± 4.2</td>
<td>7.5 ± 4.2</td>
<td>8.2 ± 3.8</td>
</tr>
<tr>
<td>RH (%)</td>
<td>80 ± 17</td>
<td>78 ± 18</td>
<td>80 ± 17</td>
<td>79 ± 20</td>
</tr>
</tbody>
</table>
Figure 1 Map of the eastern YRD region and the two observation sites, i.e., Qingpu (suburban and regional) and Pudong (urban).
Figure 2 Simplified HNO₃ formation mechanisms in the troposphere. X represents Cl, Br, and I.
Figure 3 Time series of temperature, relative humidity (RH), aerosol liquid water content (ALWC), NOx, O3, Ox, nitrogen oxidation ratio (NOR), as well as PM2.5 and major particulate compositions at the Pudong site in the winter of 2019.
Figure 4 Mass ratio of nitrate to PM$_{2.5}$ as a function of PM$_{2.5}$ concentration at (a, c) Qingpu and (b, d) Pudong sites in the winter of 2018 and 2019. The circles represent the measured ratio of NO$_3^-$/PM$_{2.5}$, and their area is linearly scaled with square root of ALWC.
Figure 5 Particulate nitrate concentration and its fraction to total nitrate ($\varepsilon_{\text{HNO}_3}$) as a function of ALWC and aerosol pH at (a, c) Qingpu and (b, d) Pudong sites in the winter of 2018 and 2019. The circles are colored according to aerosol pH.
Figure 6 Particulate nitrate concentration as a function of $[\text{NO}_2]^2[\text{O}_3]$ during the nighttime at (a, c) Qingpu and (b, d) Pudong sites in 2018 and 2019. The circles are colored according to aerosol pH and their size is linearly scaled with square root of ALWC.
Figure 7 Particulate nitrate concentration as a function of \(O_x\) during the daytime at (a, c) Qingpu and (b, d) Pudong sites in 2018 and 2019. The circles are colored according to aerosol pH and their size is linearly scaled with square root of ALWC. The data points inside the black circle in (c) correspond to low \(O_x\) levels but high ALWC and nitrate concentrations.
Figure 8 Time series of particulate nitrate, NO₂, O₃, ALWC, OH, N₂O₅, as well as the formation rate of HNO₃ from different processes during the two selected case during the pollution episodes at the Pudong site in 2019. The simulated data with RH > 95% were not included in the figure (see main text).
Figure 9 Simulated average formation rates of HNO₃ at (a) Qingpu and (b) Pudong sites during the haze pollution periods in 2019.
Figure 10 Production rates of HNO₃ from the (a) heterogeneous and (b) gas-phase processes as a function of NO₂ concentration at the Pudong site during the nighttime and daytime, respectively. The circles are colored according to the O₃ concentration in (a) and OH radical concentration in (b).
Figure 11 Average concentrations of NOx, SO2, O3, OH radicals, PM2.5, nitrate, sulfate, as well as the nitrogen and sulfur oxidation ratio (NOR and SOR) at (a-c) Pudong and (d-f) Qingpu sites before (1-22 January, 2020) and during (23 January-12 February, 2020) the COVID-19 epidemic.