Supplement of

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

Han Zang et al.

Correspondence to: Yue Zhao (yuezhao20@sjtu.edu.cn) and Yusen Duan (duanys@yeah.net)

The copyright of individual parts of the supplement might differ from the article licence.
S1. Hygroscopicity correction of aerosol volume and surface area concentrations

The hygroscopicity parameter kappa ($\kappa$) of ambient particles was estimated based on the measured chemical composition and an empirical parameterization proposed by Liu et al. (2014):

$$\kappa = 0.01 + 0.63/\text{NH}_4^+ + 0.51/\text{NO}_3^- + 0.81/\text{SO}_4^{2-} + 0.18/\text{WSOC}$$ (S1)

where $f_x$ represents the mass fraction of component $x$ in the particles. During the observation period, the mass fraction of OC in PM$_{2.5}$ was 8-13% when PM$_{2.5}$ mass concentration was above 35 $\mu$g m$^{-3}$, and the water soluble fraction (WSOC) could be smaller. Therefore, we did not consider the contribution of WSOC to $\kappa$ in our study.

According to the definition of $\kappa$ (Farmer et al., 2015), we can get the diameter of the wet particle:

$$\frac{\text{RH}}{100} = \frac{D_{p,dry}^3 - D_{p,wet}^3}{D_{p,dry}^3(1-\kappa)D_{p,dry}} \exp\left(\frac{4\sigma_\text{SA}M_w}{RT\rho_wD_{p,dry}}\right)$$ (S2)

Where $D_{p,dry}$ and $D_{p,wet}$ are the dry and wet diameters of particle, respectively; $\sigma$ is surface tension of the solution/air interface; $\rho_w$ and $M_w$ are the density and molecular weight of water; $R$ is the ideal gas constant and $T$ is the temperature (in K).

S2. The parameterization of the major heterogeneous production pathways of HONO

In this study, we parameterized the major heterogeneous HONO production pathways to estimate the HONO budget during the pollution episodes (see Table 1 in the main text). For the photolysis frequency of particulate nitrate ($j_{\text{NO}_3}$), previous studies suggested that it had a similar diurnal variation with the photolysis frequency of HNO$_3$ (Romer et al., 2018; Xue et al., 2020). Considering the fact that the photolysis rate of particulate nitrate is faster than that of HNO$_3$, an enhancement factor (EF= $j_{\text{NO}_3}/j_{\text{HNO}_3}$) was employed to parameterized the photolysis process of particulate nitrate. We also added the heterogeneous reaction between SO$_2$ and NO$_2$ on aqueous aerosols (R.S1), which is also a source of HONO in the atmosphere (Wang et al., 2016; Wang et al., 2020). In the model, the rate of this reaction was calculated using eq. S3:

$$\text{SO}_2 (g) + 2\text{NO}_2 (g) + 2\text{H}_2\text{O} (aq) \rightarrow \text{SO}_4^{2-} (aq) + 2 \text{H}^+ (aq) + 2 \text{HONO} (g)$$ (R.S1)

$$k_{SO2} = k_{aq} \times H_{\text{SO}_2} \times H_{\text{NO}_2} \times (1 + \frac{K_{a1}}{[\text{H}^+]}) + \frac{K_{a1} \times K_{a2}}{[\text{H}^+]^2}) \times \text{ALWC} \times 10^{-9}$$ (S3)

where $k_{aq}$ is the aqueous reaction rate of SO$_2$ and NO$_2$, which is $1.4 \times 10^3$ M$^{-1}$ s$^{-1}$ for pH < 5 and $2 \times 10^6$ M$^{-1}$ s$^{-1}$ for pH > 6, with a linear interpolation between the two pH values (Lee and Schwartz, 1983; Wang et al., 2020); $H_{\text{SO}_2}$ and $H_{\text{NO}_2}$ are the Henry’s Law coefficient of NO$_2$ and SO$_2$ in water, with a value of 1.23 M atm$^{-1}$ and 1.2$\times$10$^3$ M atm$^{-1}$ at 298K, respectively; $K_{a1}$ and $K_{a2}$ are the first- and second-order dissociation constant of SO$_2$-H$_2$O, with a value of 1.3$\times$10$^2$ and 6.6$\times$10$^8$ at 298K, respectively. The $H$ values at various temperatures can be derived by eq. S4:

$$H_T = H_{298} \exp\left(\frac{\Delta H_T}{R} \left(\frac{1}{298} - \frac{1}{T}\right)\right)$$ (S4)
Where $\Delta H_A$ is the enthalpy change of dissociation at constant temperature and pressure. At 298 K, the value of $\Delta H_A$ is -6.25 kcal mol$^{-1}$ for SO$_2$ and -5.0 kcal mol$^{-1}$ for NO$_2$ (Seinfeld and Pandis, 2016). $T$ is the temperature (in K).

In addition, the dissociation constant of SO$_2$·H$_2$O at different temperatures can be derived by eq. S5:

$$K_T = K_{298} \exp\left(\frac{\Delta H}{R} \left(\frac{1}{298} - \frac{1}{T}\right)\right)$$

(S5)

Where $\Delta H$ is the enthalpy change of dissociation at constant temperature and pressure. At 298 K, the value of $\Delta H$ is -4.16 and -2.23 kcal mol$^{-1}$ for dissociation of SO$_2$·H$_2$O and HSO$_3^-$, respectively (Seinfeld and Pandis, 2016).

S3. Analysis of the time series of pollutants at the Qingpu site in the winter of 2019

The time series of PM$_{2.5}$, nitrate, and other related parameters at the Qingpu site in 2019 are shown in Figure S2. The variation trends of the pollutants at the Qingpu site were similar to those at the Pudong site, but the concentrations were much higher. Nitrate was also the dominant component in PM$_{2.5}$ during the pollution episodes, and the relatively higher nitrate concentration at the Qingpu site might be due to the higher NO$_3^-$ emissions (8-263 ppb). The O$_3$ concentration ranged between 1-65 ppb with an average of 22 ppb. The O$_3$ concentration ranged from 22 to 85 ppb and was often higher than 40 ppb during the observation period. The high atmospheric oxidation capacity led to the high NOR at the Qingpu site, which was up to 0.54. Similarly, the ALWC was also high due to the high RH in the eastern YRD, and sometimes could also exceed 200 $\mu$g m$^{-3}$, which would make an important contribution to the nitrate formation.

S4. Case studies of the model simulation during the pollution episodes at the Qingpu site

Different from the Pudong site, the increase of nitrate concentration at the Qingpu site in case 1 occurred during the daytime, from 19.2 $\mu$g m$^{-3}$ at 6:00 to 39.1 $\mu$g m$^{-3}$ at 14:00 on 30 December, 2019, with an average growth rate of 2.5 $\mu$g m$^{-3}$ h$^{-1}$ (Figure S6a). The OH radical concentrations was high during the nitrate-increasing period, and the maximum values even reached $2.9 \times 10^6$ molecules cm$^{-3}$, while the N$_2$O$_5$ concentration was close to 0 ppb. This high OH concentration made the gas-phase OH + NO$_2$ process a dominant nitrate formation pathway in this case. After excluding data under RH > 95% conditions, the simulated average production rate of HNO$_3$ from the gas-phase OH + NO$_2$ process during the daytime reached 6.9 $\mu$g m$^{-3}$ h$^{-1}$.

In episode 2 (see Figure S6b), the nitrate concentration was maintained at a high level (30-40 $\mu$g m$^{-3}$) from the noon of 11 January to the midnight of 14 January, 2020. It then had a rapid increase from 36.1 $\mu$g m$^{-3}$ at 01:00 to 74.9 $\mu$g m$^{-3}$ at 10:00 on 14 January, 2020, with an average growth rate of 4.3 $\mu$g m$^{-3}$ h$^{-1}$. Similar to the Pudong site, the heterogeneous hydrolysis of N$_2$O$_5$ made the major contribution to the HNO$_3$ formation during this episode, with the average production rate of 4.0 $\mu$g m$^{-3}$ h$^{-1}$, twice that by the gas-phase process.
S5. Sensitivity analyses for key parameters of heterogeneous HONO formation and dilution process in the model

As significant uncertainties remain in the key parameters of the heterogeneous HONO formation pathways used in the model (see Table 1 in the main text), which could affect the prediction of the OH concentration and thereby HNO\textsubscript{3} production via gas-phase OH + NO\textsubscript{2} reaction, we conducted sensitivity analyses for such parameters to evaluate their influences on HNO\textsubscript{3} production during two typical pollution episodes at the Pudong site (see Figure S7). In the base case simulation where a best guess of kinetic parameters was used (see Table 1), the formation of nitrate had comparable contributions from the gas-phase and heterogeneous processes (45\% vs. 53\%) during the episode 1, while it was dominated by the heterogeneous process (79\%) during episode 2. The sensitivity analyses show that although the dark uptake coefficient of NO\textsubscript{2} on ground surfaces (γ\textsubscript{NO\textsubscript{2}-dk-gs}) had the largest influence on HONO concentration during nighttime (-40\%/+196\%, Figures S8a, d), the photo-enhanced uptake coefficient of NO\textsubscript{2} on ground surfaces (γ\textsubscript{NO\textsubscript{2}-hv-gs}) had the greatest influence on the overall HONO formation as well as HNO\textsubscript{3} production via the gas-phase process (Figures S7b, c, e, f). Specifically, varying the γ\textsubscript{NO\textsubscript{2}-hv-gs} value by a factor of 5, the gas-phase HNO\textsubscript{3} production rate had a change within -13\%/+38\% and -22\%/+63\% compared to the base scenario for the episodes 1 and 2, respectively. Correspondingly, the contribution of gas-phase processes to the total HNO\textsubscript{3} formation varied within -3\%/+8\% and -4\%/+8\%, respectively. It should be noted that variations in these kinetic parameters did not significantly affect heterogeneous HNO\textsubscript{3} production. These results suggest that the parameterizations of the heterogeneous HONO formation pathways in the model could provide robust constraints on the relative contributions of both gas-phase and heterogeneous processes to nitrate formation during haze pollution events.

Considering the uncertainty in the dilution rate constant (k\textsubscript{dil}), we also performed a sensitivity analysis for k\textsubscript{dil} by varying its value from 0.028 h\textsuperscript{-1} to 0.2 h\textsuperscript{-1} (corresponding to a dilution lifetime of 5 hours to 36 hours) to evaluate its influence on HNO\textsubscript{3} production in a typical pollution episode at the Pudong site (see Figure S8). As the dilution lifetime varied from 5 hours to 36 hours, the average concentrations of N\textsubscript{2}O\textsubscript{5} and OH radicals changed within -23\%/+0.8\% and -21.6\%/+10.8\%, respectively (Figure S8a, d), compared to the base case (dilution lifetime: 24 hours) during the episode. Accordingly, the HNO\textsubscript{3} production rates from the heterogeneous hydrolysis of N\textsubscript{2}O\textsubscript{5} and gas-phase OH + NO\textsubscript{2} reactions changed within -17\%/+1.2\% and -33\%/+12\% (Figure S8b, e) and the relative contributions of the two pathways changed within -2.5\%/+5.5\% and -5\%/+2.3\% (Figure S8c, f), respectively. The relatively small changes in the rates and relative contributions of the two HNO\textsubscript{3} production pathways upon variations in k\textsubscript{dil} from 0.028 h\textsuperscript{-1} to 0.2 h\textsuperscript{-1} suggest that the simplified parameterization of the dilution process using a constant k\textsubscript{dil} would not result in significant uncertainty in the model results.

S6. Influence of monoterpenes on HNO\textsubscript{3} production

The consumption of NO\textsubscript{3} radicals by monoterpenes during nighttime can influence the budget of NO\textsubscript{3} radicals and N\textsubscript{2}O\textsubscript{5} and thereby the formation of HNO\textsubscript{3}. We have conducted a sensitivity test for monoterpenes to evaluate their influence on the HNO\textsubscript{3} formation. It should be noted that we only have the observation data of monoterpenes obtained using a proton transfer reaction time-of-flight mass
spectrometry (PTR-ToF-MS, Vocus, Tofwerk) at an urban site in Shanghai in early November, 2019. We selected the data on 9 November as the ambient temperature (which strongly affects monoterpene emissions) on this day was relatively low (average: 13.3 °C), close to the temperature in winter. The wind speed was also low (average: 0.76 m s$^{-1}$) on this day, which limits the transport and dilution of monoterpene emissions. The monoterpene concentration on this day ranges from 0.009 ppb to 0.070 ppb, with an average of 0.038 ppb. The sensitivity analysis shows that when the monoterpene chemistry was considered, the N$_2$O$_5$ concentration and HNO$_3$ production rate from N$_2$O$_5$ hydrolysis (pHNO$_3$(N$_2$O$_5$)) both had a decrease, especially during the nighttime with high N$_2$O$_5$ concentration (Figure S9a, b). However, such decrease was relatively small; the average N$_2$O$_5$ concentration and pHNO$_3$(N$_2$O$_5$) decreased by 23% and 12% during the nighttime, respectively. In addition, the contribution of heterogeneous N$_2$O$_5$ hydrolysis to HNO$_3$ formation only decreased by 2.7% (Figure S9c). Notably, the average temperature in the selected winter haze episode was 8.1 °C, which was lower than the temperature on 9 November, so the concentration of monoterpenes may be smaller, as is their impact on the HNO$_3$ formation.
Figure S1 (a) surface area and (b) volume concentrations of dry PM$_{2.5}$ as a function of PM$_{2.5}$ mass concentration at the Qingpu site in 2019.

Figure S2 Time series of temperature, relative humidity (RH), aerosol liquid water content (ALWC), NO$_x$, O$_3$, O$_x$, nitrogen oxidation ratio (NOR), as well as PM$_{2.5}$ and major particulate compositions at the Qingpu site in winter 2019.
Figure S3 Correlation between the concentrations of PM$_{2.5}$ and nitrate, sulfate and ammonium.

Figure S4 Frequency distribution of εHNO$_3$ under different PM$_{2.5}$ pollution conditions at (a-c) Qingpu and (d-f) Pudong sites during winter 2019.
Figure S5 Time series of particulate nitrate, NO₂, O₃, ALWC, OH, N₂O₅, as well as the formation rates of HNO₃ from different processes during the two selected pollution episodes at the Qingpu site in 2019. The simulated data with RH > 95% were not included in the figure.

Figure S6 Average diurnal profile of HNO₃ production rates from the heterogeneous and gas-phase processes during all the six pollution episodes at (a) Qingpu and (b) Pudong sites.
Figure S7 Sensitivity of (a, d) HONO concentration and production rates of (b, e) HONO and (c, f) HNO$_3$ to the variations in the values of key parameters of the heterogeneous HONO formation pathways in the model. Episode 1 (a-c) was from 26 to 31 December, 2019. Episode 2 (d-f) was from 11 to 15 January, 2020. The base case was simulated using the best guess of the parameters as listed in Table 1 in the main text.

Figure S8 Sensitivity of N$_2$O$_5$ and OH radical concentrations, production rates of HNO$_3$ from different pathways, as well as their contributions to the HNO$_3$ production to the variations in the value of dilution lifetime from 5 hours to 36 hours in the model. The chosen pollution episode was from 26 to 31 December, 2019. In the base case, a typical dilution lifetime of 24 hours was assumed.
Figure S9 Sensitivity of $\text{N}_2\text{O}_5$ concentration, production rates of $\text{HNO}_3$ from $\text{N}_2\text{O}_5$ hydrolysis ($\text{pHNO}_3(\text{N}_2\text{O}_5)$), as well as its contribution to the $\text{HNO}_3$ formation ($\text{pHNO}_3(\text{N}_2\text{O}_5)/ \text{pHNO}_3(\text{total})$), to the inclusion of monoterpenes in the model simulation. The chosen episode was from 26 to 31 December, 2019. The base case did not consider the effect of monoterpenes.

Figure S10 Production rate of $\text{HNO}_3$ from the heterogeneous hydrolysis of $\text{N}_2\text{O}_5$ (the grey line with markers) as a function of $\gamma\text{N}_2\text{O}_5$ during the six haze pollution episodes at the Pudong site in the winter of 2019 (not including the data with RH > 95%). The red line is an “S” curve fitted to the $\text{HNO}_3$ production rate and the shaded area is the standard deviation. The blue circle indicates the median of $\gamma\text{N}_2\text{O}_5$ (0.022) during the six pollution episodes, which is located in the region where the heterogeneous production of $\text{HNO}_3$ is insensitive to the variation in the value of $\gamma\text{N}_2\text{O}_5$. This suggests that the uptake of $\text{N}_2\text{O}_5$ by aerosols was very efficient so that it was not the rate-determining step in the heterogeneous $\text{HNO}_3$ formation during the haze pollution periods.

References:
Liu, H. J., Zhao, C. S., Nekat, B., Ma, N., Wiedensohler, A., van Pinxteren, D., Spindler, G., Muller, K.,


