Supplement of

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

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S1. Hygroscopicity correction of aerosol volume and surface area concentrations

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

\[
κ = 0.01 + 0.63/n\text{NH}_4^+ + 0.51/n\text{NO}_3^- + 0.81/n\text{SO}_4^{2-} + 0.18/n\text{WSOC}
\]  

(S1)

where \(x\) 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 \(κ\) in our study.

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

\[
\frac{RH}{100} = \frac{D_{p,\text{wet}}^3 - D_{p,\text{dry}}^3}{D_{p,\text{wet}}^3 - (1-κ)D_{p,\text{dry}}^3} \exp\left(\frac{4σ_w M_w}{RTρ_a D_{p,\text{dry}}}\right)
\]  

(S2)

Where \(D_{p,\text{dry}}\) and \(D_{p,\text{wet}}\) are the dry and wet diameters of particle, respectively; \(σ_w\) is surface tension of the solution/air interface; \(ρ_a\) 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 H\(\text{NO}_3\) (Romer et al., 2018; Xue et al., 2020). Considering the fact that the photolysis rate of particulate nitrate is faster than that of H\(\text{NO}_3\), an enhancement factor (EF= j\(\text{NO}_3\)/jH\(\text{NO}_3\)) 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:

\[
\text{SO}_2\text{ (g)} + 2\text{NO}_2\text{ (g)} + 2\text{H}_2\text{O (aq) }→ \text{SO}_4^{2-}\text{ (aq) }+ 2\text{H}^+\text{ (aq) }+ 2\text{HONO }\text{(g)}
\]  

(R.S1)

\[
k_{120} = k_{aq} \times H_{SO2} \times H_{NO2} \times (1 + \frac{K_{a1}}{[H^+]}) + \frac{K_{a1} \times K_{a2}}{[H^+]^2}) \times \text{ALWC} \times 10^{-9}
\]

(S3)

where \(k_{aq}\) is the aqueous reaction rate of SO\(_2\) and NO\(_2\), which is \(1.4 \times 10^5\text{ M}^{-1}\text{ s}^{-1}\) for pH < 5 and \(2 \times 10^6\text{ M}^{-1}\text{ s}^{-1}\) for pH > 6, with a linear interpolation between the two pH values (Lee and Schwartz, 1983; Wang et al., 2020); \(H_{SO2}\) and \(H_{NO2}\) 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\(^2\) 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 \( \text{SO}_2 \) and -5.0 kcal mol\(^{-1}\) for \( \text{NO}_2 \) (Seinfeld and Pandis, 2016). \( T \) is the temperature (in K).

In addition, the dissociation constant of \( \text{SO}_2 \cdot \text{H}_2\text{O} \) 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 \( \text{SO}_2 \cdot \text{H}_2\text{O} \) and \( \text{HSO}_3^- \), 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 \( \text{NO}_3^- \) emissions (8-263 ppb). The \( \text{O}_3 \) concentration ranged between 1-65 ppb with an average of 22 ppb. The \( \text{O}_3 \) 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 \( \text{NOR} \) 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 \( \mu \text{g m}^{-3} \), 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 \( \mu \text{g m}^{-3} \) at 6:00 to 39.1 \( \mu \text{g m}^{-3} \) at 14:00 on 30 December, 2019, with an average growth rate of 2.5 \( \mu \text{g m}^{-3} \text{ h}^{-1} \) (Figure S6a). The \( \text{OH} \) 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 \( \text{N}_2\text{O}_5 \) concentration was close to 0 ppb. This high \( \text{OH} \) concentration made the gas-phase \( \text{OH} + \text{NO}_2 \) process a dominant nitrate formation pathway in this case. After excluding data under RH > 95% conditions, the simulated average production rate of \( \text{HNO}_3 \) from the gas-phase \( \text{OH} + \text{NO}_2 \) process during the daytime reached 6.9 \( \mu \text{g m}^{-3} \text{ h}^{-1} \).

In episode 2 (see Figure S6b), the nitrate concentration was maintained at a high level (30-40 \( \mu \text{g m}^{-3} \)) from the noon of 11 January to the midnight of 14 January, 2020. It then had a rapid increase from 36.1 \( \mu \text{g m}^{-3} \) at 01:00 to 74.9 \( \mu \text{g m}^{-3} \) at 10:00 on 14 January, 2020, with an average growth rate of 4.3 \( \mu \text{g m}^{-3} \text{ h}^{-1} \). Similar to the Pudong site, the heterogeneous hydrolysis of \( \text{N}_2\text{O}_5 \) made the major contribution to the \( \text{HNO}_3 \) formation during this episode, with the average production rate of 4.0 \( \mu \text{g m}^{-3} \text{ h}^{-1} \), 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 HNO₃ production via gas-phase OH + NO₂ reaction, we conducted sensitivity analyses for such parameters to evaluate their influences on HNO₃ 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 NO₂ on ground surfaces (γNO₂-dk-gs) had the largest influence on HONO concentration during nighttime (-40%/+196%, Figures S8a, d), the photo-enhanced uptake coefficient of NO₂ on ground surfaces (γNO₂-hv-gs) had the greatest influence on the overall HONO formation as well as HNO₃ production via the gas-phase process (Figures S7b, c, e, f). Specifically, varying the γNO₂-hv-gs value by a factor of 5, the gas-phase HNO₃ 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 HNO₃ formation varied within -3%/+8% and -4%/+8%, respectively. It should be noted that variations in these kinetic parameters did not significantly affect heterogeneous HNO₃ 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_{dil}), we also performed a sensitivity analysis for k_{dil} by varying its value from 0.028 h⁻¹ to 0.2 h⁻¹ (corresponding to a dilution lifetime of 5 hours to 36 hours) to evaluate its influence on HNO₃ 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 N₂O₅ 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 HNO₃ production rates from the heterogeneous hydrolysis of N₂O₅ and gas-phase OH + NO₂ 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 HNO₃ production pathways upon variations in k_{dil} from 0.028 h⁻¹ to 0.2 h⁻¹ suggest that the simplified parameterization of the dilution process using a constant k_{dil} would not result in significant uncertainty in the model results.

S6. Influence of monoterpenes on HNO₃ production

The consumption of NO₃ radicals by monoterpenes during nighttime can influence the budget of NO₃ radicals and N₂O₅ and thereby the formation of HNO₃. We have conducted a sensitivity test for monoterpenes to evaluate their influence on the HNO₃ 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\(_5\)O\(_5\) concentration and HNO\(_3\) production rate from N\(_2\)O\(_3\) hydrolysis (pHNO\(_3\)(N\(_2\)O\(_5\))) both had a decrease, especially during the nighttime with high N\(_2\)O\(_3\) concentration (Figure S9a, b). However, such decrease was relatively small; the average N\(_2\)O\(_3\) 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\(_3\) 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 N₂O₅ concentration, production rates of HNO₃ from N₂O₅ hydrolysis (pHNO₃(N₂O₅)), as well as its contribution to the HNO₃ formation (pHNO₃(N₂O₅)/pHNO₃(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 HNO₃ from the heterogeneous hydrolysis of N₂O₅ (the grey line with markers) as a function of γN₂O₅ 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 HNO₃ production rate and the shaded area is the standard deviation. The blue circle indicates the median of γN₂O₅ (0.022) during the six pollution episodes, which is located in the region where the heterogeneous production of HNO₃ is insensitive to the variation in the value of γN₂O₅. This suggests that the uptake of N₂O₅ by aerosols was very efficient so that it was not the rate-determining step in the heterogeneous HNO₃ formation during the haze pollution periods.

References:
Farmer, D. K., Cappa, C. D., and Kreidenweis, S. M.: Atmospheric Processes and Their Controlling Influence on Cloud Condensation Nuclei Activity, Chem. Rev., 115, 4199-4217, https://doi.org/10.1021/cr5006292, 2015.
Lee, Y., and Schwartz, S. E.: Kinetics of oxidation of aqueous sulfur (IV) by nitrogen dioxide, in Precipitation Scavenging, Dry Deposition and Resuspension, Proceedings of the Fourth International Conference, Santa Monica, California, 29 November–3 December 1982, edited by H. Pruppacher, R. Semonin, and a. W. G. N. Slinn, pp. 453–470, Elsevier, New York.
Liu, H. J., Zhao, C. S., Nekat, B., Ma, N., Wiedensohler, A., van Pinxteren, D., Spindler, G., Muller, K.,
and Herrmann, H.: Aerosol hygroscopicity derived from size-segregated chemical composition and its parameterization in the North China Plain, Atmos. Chem. Phys., 14, 2525-2539, https://doi.org/10.5194/acp-14-2525-2014, 2014.

Romer, P. S., Wooldridge, P. J., Crounse, J. D., Kim, M. J., Wennberg, P. O., Dibb, J. E., Scheuer, E., Blake, D. R., Meinardi, S., and Brosius, A. L.: Constraints on Aerosol Nitrate Photolysis as a Potential Source of HONO and NOx, Environ. Sci. Technol., 52, 13738-13746, https://doi.org/10.1021/acs.est.8b03861, 2018.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to climate change, Third edition. ed., John Wiley & Sons, Inc., Hoboken, New Jersey, xxvi, 1120 pages pp., 2016.

Wang, G., Zhang, R., Gomez, M. E., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-Ortiz, W., Secrest, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss, P. S., Duce, R. A., Kolb, C. E., and Molina, M. J.: Persistent sulfate formation from London Fog to Chinese haze, Proc. Natl. Acad. Sci. USA, 113, 13630-13635, https://doi.org/10.1073/pnas.1616540113, 2016.

Wang, J., Li, J., Ye, J., Zhao, J., Wu, Y., Hu, J., Liu, D., Nie, D., Shen, F., Huang, X., Huang, D. D., Ji, D., Sun, X., Xu, W., Guo, J., Song, S., Qin, Y., Liu, P., Turner, J. R., Lee, H. C., Hwang, S., Liao, H., Martin, S. T., Zhang, Q., Chen, M., Sun, Y., Ge, X., and Jacob, D. J.: Fast sulfate formation from oxidation of SO2 by NO2 and HONO observed in Beijing haze, Nat. Commun., 11, 2844, https://doi.org/10.1038/s41467-020-16683-x, 2020.

Xue, C., Zhang, C., Ye, C., Liu, P., Catoire, V., Krzyztopiak, G., Chen, H., Ren, Y., Zhao, X., Wang, J., Zhang, F., Zhang, C., Zhang, J., An, J., Wang, T., Chen, J., Kleffmann, J., Mellouki, A., and Mu, Y.: HONO Budget and Its Role in Nitrate Formation in the Rural North China Plain, Environ. Sci. Technol., 54, 11048-11057, https://doi.org/10.1021/acs.est.0c01832, 2020.