Dear Editor and Referee

Thank you for reviewing and commenting upon our manuscript, "Elucidate the Formation Mechanism of Particulate Nitrate Based on Direct Radical Observations in Yangtze River Delta summer 2019" by Tianyu Zhai et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-548-RC1, 2022. As detailed below, the reviewer's comments are in italicized font, and our responses to the comments are in regular font. New or modified text is in blue.

For concerns from Referee 1

We've responded to each comment individually below and would like to draw your attention to two major concerns:

Comment 1:

Using a constant coefficient for the whole campaign seems to be less convincing, although 0.035 was a reasonable value in this area. I suggest to perform some uncertainty tests or at least choose different coefficient for clean days and polluted days, respectively, as the aerosol composition and water content were not supposed to be the same.

Reply: We thank for these constructive comments and suggestions to improve the quality of our manuscript. In the article, we add the timeseries and box-whisker plots of γ_p for clean days and polluted days, respectively (Figure 6). The average γ_p is 0.069 ± 0.0050 in polluted condition and 0.0036 ± 0.0026 in clean condition. Moreover, the different values γ_p will be applied to subsequent nitrate formation contribution calculation. More clarifications have been added in section 3.3 as follows：

The other approach is the parameterization by (Yu et al., 2020) which depicted as follows:

$$\gamma_P = \frac{4}{c}\frac{V_a}{S_a} K_H \times 3.0 \times 10^4 \times [H_2O] \left(1 - \frac{1}{\left(0.033 \times \frac{[H_2O]}{[NO_3^-]}\right) + 1 + \left(3.4 \times \frac{[Cl^-]}{[NO_3^-]}\right)}\right) \quad \text{Eq11}$$

where V_a/S_a is the measured aerosol volume to surface area ratio by SMPS; K_H is Henry's law coefficient which is set as 51 as recommended; $[NO_3^-]$ and $[Cl^-]$ are

aerosol inorganic concentration measured by Marga; [H_2O] is aerosol water content calculated through ISORROPIA II. The valid parameterization calculated N_2O_5 uptake coefficient (note as γ_P) from May 30th to June 08th, 2019 shows in Figure 6, there is a good consistency between the trends of γ_P and aerosol water content. Nighttime γ_P varys from 0.001 to 0.024 with average 0.069 ± 0.0050 on polluted condition and 0.0036 ± 0.0026 on clean condition. the N_2O_5 uptake coefficient shows good correlation to RH and aerosol water content. For N_2O_5 uptake coefficient, although particulate nitrate mass concentration increased during pollution event, antagonistic effect on N_2O_5 uptake coefficient was not obvious for the nitrate molarity decreasing.

Furthermore, we compare the difference between γ_S and γ_P[h]. Taking the night of May 30th as example, the γ_S is 0.089 while γ_P ranges from 0.024 to 0.057 with average value as 0.013 ± 0.0051. The difference between steady-state and parameterization is significant, one possible explain is uncertainty for stationary-state approximation caused by local NO or VOCs emission (Brown et al., 2009; Chen et al., 2022). Another reason is parameterization by Yu et al. ignore the impact from organic matter on fine particle. The difference aerosol composition between this work and Yu et al may also bring uncertainty. Overall consideration, γ_P will be chosen for N_2O_5 heterogeneous uptake coefficient in later analysis and discussion.

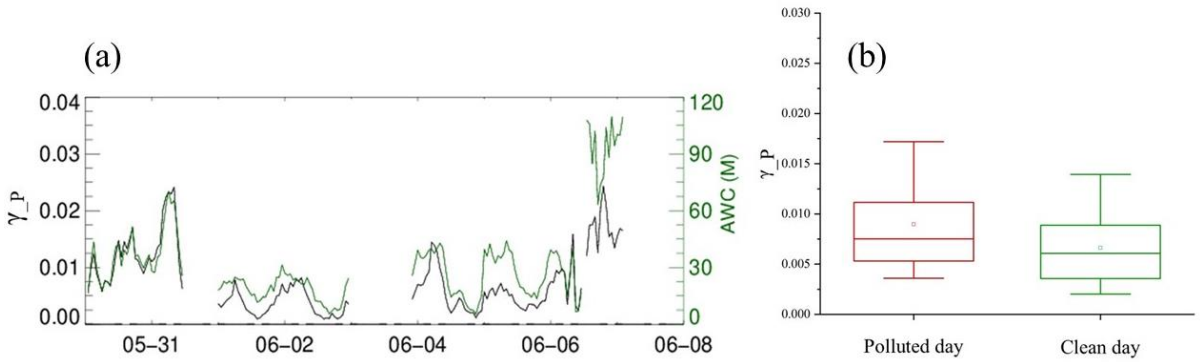

Figure 6 Results of N_2O_5 uptake coefficients through parameterization (γ_P). (a) shows timeseries of γ_P and ISORROPIA II results of aerosol water content (AWC). (b) is the box-plot of γ_P on polluted day and clean day, hollow square represents the mean value and the solid line across the box shows the median score for the data set, while the top and bottom whiskers represent 90 % and 10 % value of γ_P, respectively.

Comment 2: *Please explain the reason for the significant difference between gamma_s and gamma_p.*

Reply: First, local NO or VOCs emission during nighttime will break steady chemical condition for stationary-state approximation as the temperature and kNO_3 meet requirements reported in the literature (Brown et al., 2009; Chen et al., 2022). What's more, the ignorance of organic matter influence on N_2O_5 heterogeneous uptake coefficient in parameterization will also bring uncertainty.

Word and format problems have been corrected as suggested for other specific comments.

Line 91 change "impact factor" to "controlling factors"

Line 241 change 'appeal" to "appear"

The conclusion at lines 276~279 has been deleted for no more evidence.

For concerns from Referee 2

We've responded to each comment individually below and would like to draw your attention to two major concerns:

Comment 1: About Line 75-77 and Line 275-276, the concern about the contribution of NO_2 heterogeneous uptake.

Reply: Thanks for this precious advice. First, we change the description of NO_2 heterogeneous uptake contribution on nitrate formation and add relative literature reports around line 75. What's more, the NO_2 heterogeneous uptake pathway analysis has been added to chapter 3.4. The NO_2 uptake coefficient is set as 5.8×10^{-6} depending on the report by Yu et al. (2021), which is the result of 70% RH on urban grime. The NO_2 heterogeneous uptake pathway contribution on nitrate formation mass increased twice on polluted day than on clean day. However, there remains a distance among the value of NO_2 heterogeneous uptake, $OH+NO_2$, and N_2O_5 heterogeneous uptake. More

clarifications have been added in section 3.3 as follows：

As shown in Figure 7c, OH + NO_2 dominates nitrate production on clean day, while the N_2O_5 uptake pathway only contributes 13.6 μg m^{-3}. On polluted days, the ability of N_2O_5 uptake grows fast which reached 50.1 μg m^{-3}, while OH pathway doesn't change too much. There is no distinct difference of daytime pathway (OH + NO_2) between clean day and polluted day, while the nighttime pathway ratio rises from 38.1 % on clean day to 67.2 % on polluted day.NO_2 heterogeneous uptake increases from 0.93 μg m^{-3} on clean day to 2.0 μg m^{-3} on polluted day, but the contribution proportion do not change obviously. Both the higher N_2O_5 uptake coefficient and higher S_a on polluted day increase the contribution of N_2O_5 hydrolysis on particular nitrate at pollution condition.

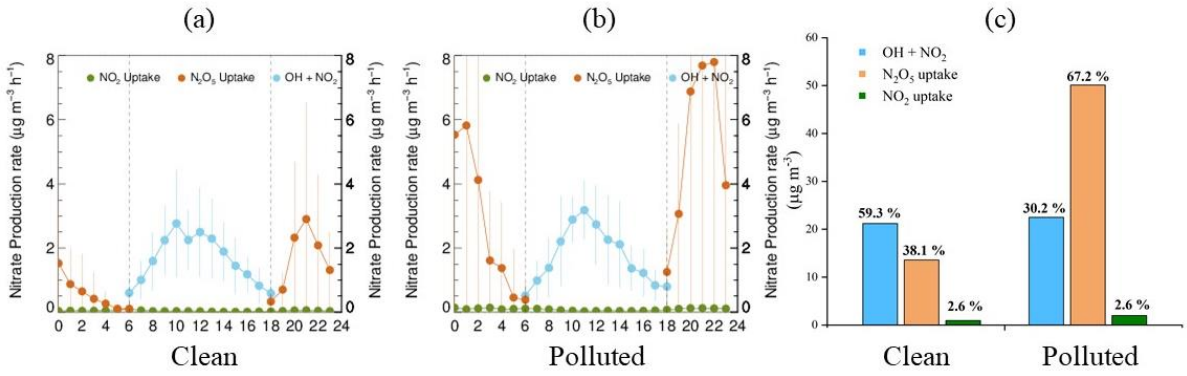

Figure 7 The mean diurnal variations of nitrate production potential of clean day(a) and polluted day (b) and the P(NO_3^-) distribution of clean and polluted day (c).

Comment 2: What does the "water-soluble ion" refer to?

Reply: "water-soluble ion" refer to Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, NO_3^-, Cl^- and SO_4^{2-} components in particle. In order to avoid confusion, "water-soluble particulate components" is used to replace all the "water-soluble ion".

Comment 3: Can the author elaborate more on the NOR difference between PD and CD? From my perspective, particular factors should lead to such a discrepancy. Any suggestions?

Reply: The NOR increased during PD reveals the fast transformation of NO_2 to NO_3^-, which is in accordance with nitrate ratio explosive growth during PD. As discussed in chapter 3.4, both the N_2O_5 heterogeneous uptake pathway and NO_2 heterogeneous uptake pathway increased more than twice during PD. In our opinion, there is no significant difference in the RH, NO_2 concentration, and N_2O_5 concentration between PD and CD. Even the N_2O_5 concentration decreased during PD night. The nitrate formation contribution increase is controlled by the aerosol surface growth and aerosol water content increase which is due to the change of particulate composition.

Comment 4: Any suggestions on the increased ability of N_2O_5 uptake on a polluted day? Is it due to the different composition of particles on PD and CD? Need more elaboration.

Reply: Both the higher N_2O_5 uptake coefficient and higher S_a on polluted day increase the contribution of N_2O_5 hydrolysis on particular nitrate at pollution condition. Both the N_2O_5 uptake coefficient and S_a shows a good correlation to RH and aerosol water content. For the N_2O_5 uptake coefficient, although particulate nitrate mass concentration increased during pollution event, antagonistic effect on N_2O_5 uptake coefficient was not obvious for the nitrate molarity decreasing.

Thank you again for your thoughtful comments.

Reference

Brown, S. S., Dube, W. P., Fuchs, H., Ryerson, T. B., Wollny, A. G., Brock, C. A., Bahreini, R., Middlebrook, A. M., Neuman, J. A., Atlas, E., Roberts, J. M., Osthoff, H. D., Trainer, M., Fehsenfeld, F. C., and Ravishankara, A. R.: Reactive uptake coefficients for N2O5 determined from aircraft measurements during the Second Texas Air Quality Study: Comparison to current model parameterizations, Journal of Geophysical Research-Atmospheres, 114, 10.1029/2008jd011679, 2009.

Chen, X., Wang, H., and Lu, K.: Interpretation of NO3-N2O5 observation via steady state in high-aerosol air mass: the impact of equilibrium coefficient in ambient conditions, Atmospheric Chemistry and Physics, 22, 3525-3533, 10.5194/acp-22-3525-2022, 2022.

Yu, C., Wang, Z., Xia, M., Fu, X., Wang, W. H., Tham, Y. J., Chen, T. S., Zheng, P. G., Li, H. Y., Shan, Y., Wang, X. F., Xue, L. K., Zhou, Y., Yue, D. L., Ou, Y. B., Gao, J., Lu, K. D., Brown, S. S., Zhang, Y. H., and Wang, T.: Heterogeneous N2O5 reactions on atmospheric aerosols at four Chinese sites: improving model

representation of uptake parameters, Atmospheric Chemistry and Physics, 20, 4367-4378, 10.5194/acp-20-4367-2020, 2020.