

## Referee #2

The authors present two-years measurements of fine nitrate aerosol at a rural site in the Yangtze River Delta, China. The data are analyzed to illustrate the seasonal and diurnal variations of particulate nitrate and its formation pathways. It was found that photochemical formation of nitric acid and its thermodynamic equilibrium with  $\text{NO}_3^-$  play a dominant role in summer, whilst hydrolysis of  $\text{N}_2\text{O}_5$  dominates in winter. Overall, this study provides valuable observational data and useful insights into the chemical behaviors of nitrate aerosol in the polluted atmospheres of China. Thus this manuscript can be accepted for publication after the following comments are properly addressed.

Specific comments:

The major concern is on the steady state calculation of  $\text{N}_2\text{O}_5$  and its contribution to the  $\text{NO}_3^-$  formation. First, is the steady state assumption valid in this study, especially for the cold conditions in winter? The authors need estimate the chemical lifetimes of  $\text{N}_2\text{O}_5$  for the selected cases and examine if the air masses were in steady state for  $\text{N}_2\text{O}_5$ ? Some parameters (e.g., uptake coefficient of  $\text{N}_2\text{O}_5$  onto particles) are highly uncertain, which may introduce large uncertainty to the calculation. The chemical loss of  $\text{NO}_3$  radical via reaction with VOCs is also highly variable and depends on the abundances and chemical speciation of VOCs, especially biogenic VOCs. The authors may conduct more calculations with varying levels of uptake coefficients and reaction rates of  $\text{NO}_3^-$ +VOCs, to examine the sensitivity of the major conclusions to these assumptions.

Response: Thanks, we agree with the referee's comment.

We calculated the chemical lifetimes of  $\text{N}_2\text{O}_5$  using the method described in (Brown et al., 2006 and Brown et al., 2016). The average chemical lifetimes of  $\text{N}_2\text{O}_5$  for the selected cases is about 0.1(0.006-0.3) hour, mostly less than 10 minutes (>75%). Air mass of the selected cases were relative stable with low wind speed and consistent wind direction. Therefore, we believed the steady state method can be used in this study.

The uptake coefficient of  $\text{N}_2\text{O}_5$  and the chemical speciation of VOCs can really cause uncertainty. The details of the calculation and the uncertainty to the result will be discussed in support information. We will add the result of uncertainty calculation in the revised manuscript.

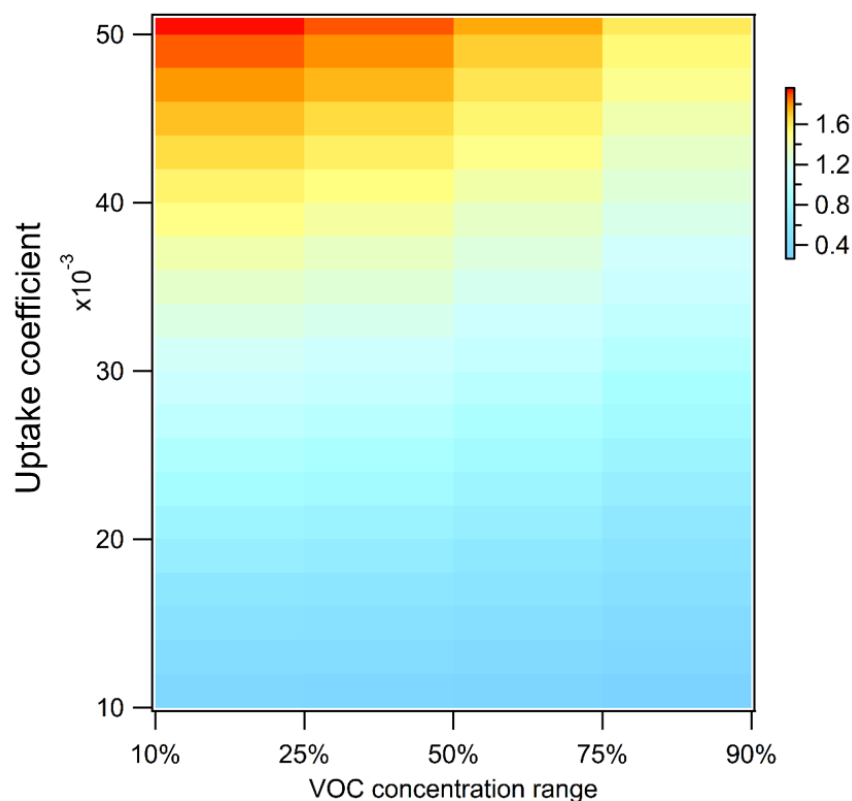


Fig. S5 The uncertainty of the calculation of nitrate from hydrolysis of N<sub>2</sub>O<sub>5</sub> with varying levels of uptake coefficients and reaction with different VOCs. It should be noted that the figure is color-coded by the ratio of nitrate produced by hydrolysis of N<sub>2</sub>O<sub>5</sub> with different levels of uptake coefficients and VOCs to the nitrate produced by hydrolysis of N<sub>2</sub>O<sub>5</sub> with the parameter used in the paper section 2.4. The X axis presents the different VOC percentiles.

*Brown, S. S., Ryerson, T. B., Wollny, A. G., Brock, C. A., Peltier, R., Sullivan, A. P., Weber, R. J., Dube, W. P., Trainer, M., Meagher, J. F., Fehsenfeld, F. C., and Ravishankara, A. R.: Variability in nocturnal nitrogen oxide processing and its role in regional air quality, Science, 311, 67-70, 2006.*

*Brown, S. S., Dube, W. P., Tham, Y. J., Zha, Q. Z., Xue, L. K., Poon, S., Wang, Z., Blake, D. R., Tsui, W., Parrish, D. D., and Wang, T.: Nighttime chemistry at a high altitude site above Hong Kong, J Geophys Res-Atmos, 121, 2457-2475, 10.1002/2015JD024566, 2016.*

Section 3.1: although this manuscript focused on fine particulate nitrate, it should be useful to document the overall measurement results of other related species, such as sulfate, PM<sub>2.5</sub>, NO<sub>x</sub>,

O<sub>3</sub> and NH<sub>3</sub>. Besides the ratio of nitrate to water-soluble ions, it is also very useful to show the mass ratio of nitrate to PM<sub>2.5</sub>.

Response: Thanks for the comment.

Seasonal sulfate concentrations have been drawn in Fig.4. The overall statistical results of other related species will be added to table S2. We will add table S2 in the revised support information,

Comments from Referees: Pg 3, Lines 64-66: the following recent observational studies of N<sub>2</sub>O<sub>5</sub> in China should be acknowledged here.

Response: Thanks for the comment. The references will be added in the revised manuscript.

Comments from Referees: Pg 9, Lines 230-233: it should be noted here that these trends were derived from various observations obtained from different sites in the specific regions, other than from long-term observations at the same site.

Response: Thanks for the comment. We agree the trend shown in Fig.1 were not guarantee. We will modify the statement in the revised manuscript as follows.

*“Third, an overall increasing trend of particulate nitrate was implied in NCP and YRD in the past decade, especially that during summertime.”*

*“It should be noted that these measurements were from various observations obtained from different sites in specific regions other than from long-term observations at the same site. These conclusions we acquired from limited literature records should have considerable uncertainty.”*

Comments from Referees: Pg 23, Lines 666-669: cite the final ACP paper instead.

Response: Thanks for your reminder. The reference will be replaced in the revised manuscript.

Comments from Referees: Figure 1: the above reference (Wen et al., 2018) has reported very recent observations of fine particulate nitrate at three different sites (urban, rural and mountain sites) in the North China Plain. It would be useful to include these recent data in Figure 1 for comparison.

Response: Thanks for your suggestion. We will add the information in the Fig.1 in the revised

manuscript.

Comments from Referees: Figure 4: is the nitrate/sulfate ratio mass-based or molar-based? The molar ratio of nitrate to sulfate should be better here.

Response: Thanks for the comment. The original ratio in the Fig.4 is mass-based and we will replace it with the molar-based ratio in the revised manuscript.

Comments from Referees: Figure 9: please provide a legend for the wind vectors.

Response: Thanks for the comment, and will add a legend for the wind vectors.

Comments from Referees: Table 1: it should be helpful to provide the exact values of these rate constants used in this study.

Response: Thanks for your suggestion. We will add them into the Ttable1 in the revised paper.