

Interactive comment on “Nitrate formation from heterogeneous uptake of dinitrogen pentoxide during a severe winter haze in southern China” by Hui Yun et al.

Anonymous Referee #3

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The manuscript “Nitrate formation from heterogeneous uptake of dinitrogen pentoxide during a severe winter haze in southern China” by Yun and Co-authors uses observations of aerosol and gases and model results to study the contribution of heterogeneous chemistry via N_2O_5 to nitrate formation in $\text{PM}_{2.5}$ during severe winter haze episodes. The measurements were carried out in the rural site of Hesnan, located near the Pearl River Delta in Southern China. In addition to a comprehensive suite of measurements, Yun and co-authors present the results of a chemical box model to estimate daytime HNO_3 mixing ratios. The box model was constrained by observations and its results were used to assess the importance of nighttime N_2O_5 over daytime HNO_3 as source of secondary aerosol nitrate.

C1

The paper is well written, well structured and conveys results of interest for the scientific community. However, the method section (as pointed out by Referees #1 and #2 as well) has to be improved and that some more discussion on 1) uncertainties, 2) sensitivity test of the model and 3) boundary layer dynamic needs to be added before publication.

1) The description of the measurements should include the detection limits and the uncertainties, in particular for the species that were used to constrain the chemical box model. 2) There should be a discussion in the main text or in the SI about the sensitivity of the box model to the uncertainties of the measurements (this, for example should be communicated with uncertainty bars in figure 7). 3) In paragraph 2.2 a discussion about interference for species with the same nominal mass as $\text{I}(\text{N}_2\text{O}_5)$ - and $\text{I}(\text{ClNO}_2)$ - should be added. How much contribution from other species would Yun and Co-authors expect? If it was not negligible how would change the results from the box model/comparison? 4) Relative humidity (RH) is known to affect measurements carried out with I-CIMS. Was the inlet used in this study humidified? Was the RH controlled/monitored during zero measurements? How could the zero affect the box model results (e.g., over/under estimation of $\text{N}_2\text{O}_5/\text{ClNO}_2$)? What are the biases that the 6 m sampling line could generate in their results? 5) The boundary layer plays a significant role in the time evolution of the concentrations of nitrate in the particle. Yun and Co-authors make little to no mention of its role. For example, one might expect that particulate nitrate would increase also in the early morning hours due to the contribution of the residual layer during the mixing. This doesn't seem to happen in the observations presented in this work. May the Authors discuss why that would be the case? 6) An increase in particulate nitrate concentrations (as well as $\text{PM}_{2.5}$) could also be due to a dilution effect (same magnitude of aerosol sources but reduced volume in which the aerosols are mixed). I recommend adding a few sentences explaining how the mixing of the residual layer in the morning hours could affect the results presented here.

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