

# ***Interactive comment on “Two years online measurement of fine particulate nitrate in western Yangtze River Delta: Influences of thermodynamics and N<sub>2</sub>O<sub>5</sub> hydrolysis” by Peng Sun et al.***

## **Anonymous Referee #1**

Received and published: 9 August 2018

This paper reports aerosol composition, its seasonal cycle, its correlation with other trace gases, and an analysis of chemical mechanisms responsible for particulate nitrate formation from a site in the Yangtze River Delta (YRD) of China during two years of continuous measurements at hourly time resolution. The data set and analysis appear to be unique, and their presentation represents a new contribution that will be of interest to the readership of ACP. The paper will add to the growing literature on the characteristics of nitrate aerosol in China. I recommend publication following attention to the comments and technical corrections below.

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## Minor comments

Line 69: The daytime concentration of N<sub>2</sub>O<sub>5</sub> cannot always be neglected. In some cases, there is evidence that it leads to relatively rapid soluble nitrate production. See Figure 14 in:

Brown, S.S., W.P. Dubé, Y.J. Tham, Q. Zha, L. Xue, S. Poon, Z. Wang, D.R. Blake, W. Tsui, D.D. Parrish, and T. Wang, Nighttime chemistry at a high altitude site above Hong Kong. *Journal of Geophysical Research: Atmospheres*, 2016. 121(5): p. 2457-2475.

Line 71: The direct water vapor reaction is much slower than heterogeneous uptake and can generally be neglected. The last line in Table 1 shows this reaction using the Wahner parameterization. This parameterization has been shown to be inconsistent with field measurements of N<sub>2</sub>O<sub>5</sub>.

Crowley, J.N., J. Thieser, M.J. Tang, G. Schuster, H. Bozem, Z.H. Beygi, H. Fischer, J.M. Diesch, F. Drewnick, S. Borrmann, W. Song, N. Yassaa, J. Williams, D. Pöhlner, U. Platt, and J. Lelieveld, Variable lifetimes and loss mechanisms for NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> during the DOMINO campaign: contrasts between marine, urban and continental air. *Atmos. Chem. Phys.*, 2011. 11(21): p. 10853-10870.

Brown, S.S., W.P. Dubé, H. Fuchs, T.B. Ryerson, A.G. Wollny, C.A. Brock, R. Bahreini, A.M. Middlebrook, J.A. Neuman, E. Atlas, M. Trainer, F.C. Fehsenfeld, and A.R. Ravishankara, Reactive uptake coefficients for N<sub>2</sub>O<sub>5</sub> determined from aircraft measurements during TexAQS 2006; Comparison to current model parameterizations. *J. Geophys. Res.*, 2009. 114: p. D00F10.

Line 195-197: There is not much basis for the assumption of equal NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> loss rate constants. It would be useful for the authors to also give the average ambient NO<sub>2</sub> level, and the associated average ratio of N<sub>2</sub>O<sub>5</sub> to NO<sub>3</sub> calculated from equilibrium. If this ratio is large, then one could argue (with some basis) that N<sub>2</sub>O<sub>5</sub> reactions are likely to be more important than NO<sub>3</sub> reactions. Also, what does the symbol “i” represent in

the NO<sub>3</sub> uptake expression in Table 1?

Lines 230-233: The trends in nitrate are not evident in Figure 1. To which data do the statements about trends refer?

Line 251: Replace “around 0 C” with a statement of upper and lower bounds, i.e., -5 to +5 C or whatever range defines this percentage of nitrate.

Line 257: The equation in the text line does not make sense. Authors should check for accuracy. Furthermore, it is rare that excess ammonium is observed in the particle phase. Is this what the authors mean to say?

Line 258-262: The seasonal differences referred to here are not apparent in the way the data are presented in Figure 3b. Are the authors invoking Ca, K and Cl to explain the variation of the darker and warmer colors with respect to the fit line? If so, the writing is not clear. If not, then the data for C, K and Cl should be shown.

Line 270: The bimodal pattern is not obvious in sulfate. There does not appear to be a peak in January. If the data were displayed with the y-axis from zero, there would seem to be very little seasonal variation in sulfate. This observation is itself in contrast to other polluted regions (Europe, US), which show a strong summertime maximum in sulfate.

Lines 287-289: Writing is unclear. Is the NO<sub>x</sub> decrease from Jan – Feb caused by a festival? It would seem more likely to be caused by meteorology / BL depth / transport, etc., but the cause and effect with the festival is implied but not stated. The attribution to factors other than local emissions is therefore not clearly made. Grammar also needs correcting: “It might suggest” should be replaced by “The observations might suggest”. Even with the grammar correction, the case for the attribution here is not clear.

Line 290-299: The results of the equilibrium calculation do not make sense. HNO<sub>3</sub> is a calculated quantity from the equilibrium. If so, then the points should all lie either exactly on the lines or below it, but not above, since HNO<sub>3</sub> above the line would be

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calculated to be in the aerosol phase. How was the calculation of  $\text{HNO}_3$  done, and how does it lead to points that are not in equilibrium under conditions where the aerosol is favored? Also, the plots would be better displayed with the y-axis on a log scale to better illustrate the behavior at low temperature, especially in winter.

Line 327: Brown and Dube 2007 is not the best reference here with respect to particulate nitrate. Baasandorj et al. 2017 is a good reference, however.

Baasandorj, M., S.W. Hoch, R. Bares, J.C. Lin, S.S. Brown, D.B. Millet, R. Martin, K. Kelly, K.J. Zarzana, C.D. Whiteman, W.P. Dubé, G. Tonnesen, I.C. Jaramillo, and J. Sohl, Coupling between Chemical and Meteorological Processes under Persistent Cold-Air Pool Conditions: Evolution of Wintertime  $\text{PM}_{2.5}$  Pollution Events and  $\text{N}_2\text{O}_5$  Observations in Utah's Salt Lake Valley. *Environmental Science & Technology*, 2017. 51(11): p. 5941-5950.

Line 354-355: The influence of thermodynamics is not smaller in winter compared to summer. Perhaps the authors mean that it has a smaller influence on the diurnal cycle?

Line 364: Does “percent” mean “percentile”? The text does not make the choice of 25th percentile clear, nor that the selection is for top and bottom percentages. The figure 8 caption is clear. Text should read more like the figure caption.

Line 371-372: The retroplume in Figure S3 does not overlap with the biomass burning region. Does this imply that the region with high biomass burning gives rise to lower nitrate concentrations? What is the overlap of the lower 25th percentages with the biomass burning regions?

Line 432-433: The product of  $\text{NO}_2 \cdot \text{O}_3$  is a proxy for the  $\text{N}_2\text{O}_5$  production rate, but this could be calculated quantitatively in units such as molecules  $\text{cm}^{-3} \text{s}^{-1}$  or ppbv  $\text{hr}^{-1}$  quite easily by also multiplying by the  $\text{NO}_2 + \text{O}_3$  rate constant. This would be more intuitive in Figure 10.

Technical corrections

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Line 49: the Chinese government

Line 68: the N<sub>2</sub>O<sub>5</sub> concentration

Line 79 (and 89): do the authors mean “undenuded” rather than “undenude” ?

Line 85: suggest to replace “super” with either “rather” or “extremely”

Line 107: Please specify which Zhang reference (a, b or c)

Line 113: “of” in place of “on”

Line 239: “ranges” instead of “range”

Line 248: Suggest to replace “They overall overall correlated to each other with correlation coefficient . . .” with “The correlation coefficient was . . .”

Line 256: replace “contrasts with” with “in contrast with”

Line 280: eliminate the word “commendably”

Line 291: “calculate” rather than “calculated”

Line 312: replace “prefer to evaporate and dilute the particulate nitrate” with “lead to evaporation and dilution of the particulate nitrate.”

Line 316: “The equilibrium constant”

Line 319: Suggest replacing “was highly correlated to” with “showed the same diurnal pattern as”

Line 321: Replace “considerable” with “moderate” and eliminate the word “appeared”

Line 335: replace “were showed” with “are shown”

Line 345: “neglected” in place of “ignored”

Line 349: “product of NO<sub>2</sub>” rather than “production of NO<sub>2</sub>”. Also insert “the” before “production rate of nitric acid”

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Line 367: “be associated with” rather than “accompany with”

Line 399: the steady state approximation

Line 405: “approximately” in place of “approximate”

Line 419: remove the word “has”

Line 450: , and ammonium nitrate

Line 453: contributed to the nitrate

Line 457: the ISORROPIA II model

Line 459: the biomass burning regions

Line 459: Replace “corresponded to” with “associated with”

Line 460: the North China Plain

Line 466: replace “and” with “which”

Line 470: use the phrase “and this residual layer nitrate will contribute”

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-608>, 2018.

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