Referee #1

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.

Minor comments

Line 69: The daytime concentration of N2O5 cannot always be neglected. In some cases, there is evidence that it leads to relatively rapid soluble nitrate production.

Response: Yes, we agree that N2O5 cannot be always ignored, especially during the polluted or cloudy days. We will modify the description it in the revised manuscript.

"Due to the rapid photolysis of NO_3 radical, the contribution of N_2O_5 hydrolysis to nitrate concentration during daytime of sunny day is usually small."

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 N2O5.

Response: Thanks to the comment. We agree that the direct water vapor reaction can be neglected compared with the heterogeneous uptake of N2O5. We will remove it in the revised manuscript.

Line 195-197: There is not much basis for the assumption of equal NO3 and N2O5 loss rate constants. It would be useful for the authors to also give the average ambient NO2 level, and the associated average ratio of N2O5 to NO3 calculated from equilibrium. If this ratio is large, then one could argue (with some basis) that N2O5 reactions are likely to be more important than NO3 reactions. Also, what does the symbol "i" represent in the NO3 uptake expression in Table 1?

Response: Thanks for the comment. We will add the NO2 level in the revised manuscript.

We did not have the VOCs measurement during the two-year period, but continuously VOCs measurement using PTR-TOF after 2017. The VOCs data we used in the manuscript was the averaged value measured at SORPES site, which is believed to be a reasonable value. In the revised manuscript, we will recalculate the result about N2O5, and evaluate the uncertainty caused by the uptake coefficient of N2O5 and different levels of VOCs, and will add the information in the support information. We will modify the statement in the revised manuscript.

There should be no symbol "i" in that position in Table 1. Thanks for your reminder.

Lines230-233: The trends in nitrate are not evident in Figure 1. To which data do the statements about trends refer?

Response: Thanks for the comment. We agree that the trends shown in Fig. 1 are not evident, and will modify the statement in the revised manuscript as follows. The related data and references are listed in Table S1. We will modify the description it in the revised manuscript.

"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."

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.

Response: Thanks for the comment. We will modify it into the revised manuscript.

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?

Response: Thanks for the comment. Here, excess ammonium is defined as the amount of ammonium in excess of that required for satisfying $[NH_4^+]/[SO_4^{2-}] = 1.5$. The reference is below. If there is not

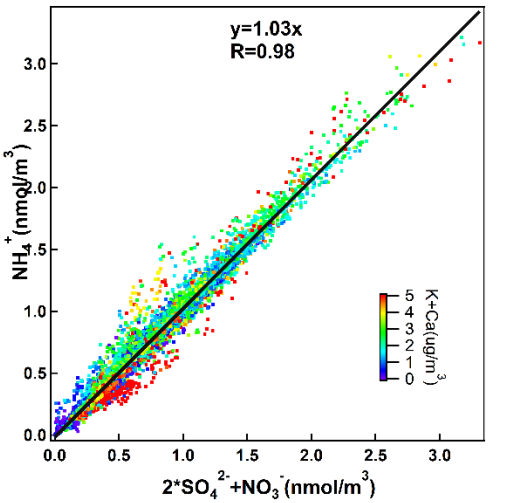
enough ammonia in the atmosphere, the ammonia tends to react with sulfuric acid and form ammonium hydrogen sulfate first. Then the possibility of ammonia react with nitric acid or ammonium hydrogen sulfate is almost the same. However, here we wanted to express the difference between two sites. The expression is not very proper and we will correct it in the revised manuscript.

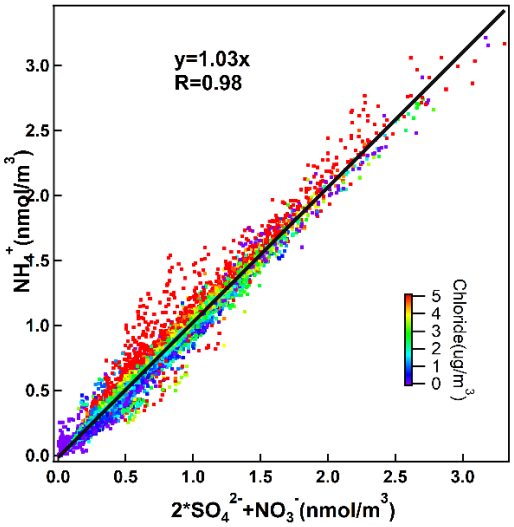
Griffith, S. M., Huang, X. H. H., Louie, P. K. K., and Yu, J. Z.: Characterizing the thermodynamic and chemical composition factors controlling PM2.5 nitrate: Insights gained from two years of online measurements in Hong Kong, Atmospheric Environment, 122, 864-875, 10.1016/j.atmosenv.2015.02.009, 2015.

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.

Response: Thanks for the comment. We did not invoke Ca, K and Cl in Fig.3, but in the following figure. High concentrations of Cl can be observed at lower temperature condition. The data points would be below the regression line, when the concentrations of Ca and K were high for some special process in early summer such as dust and biomass burning. We will modify the statement in the revised manuscript.

"In spring and early summer, a fraction of the particulate nitrate is present in the forms of $Ca(NO_3)_2$ and KNO_3, which is the explanation of the points below the regression line in Fig. 3b; while in winter, considerable chloride would consume some ammonia to form NH_4Cl (Hu et al., 2017), resulting in the points below the regression line especially in winter."





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.

Response: Thanks for the comment. We agree that the peak of sulfate in January is not evident. In China, there are usually more SO_2 emissions during heating season (winter), especially in northern China. Sulfate concentrations at our site should be influenced by the air masses form Northern China during winter. However, during summer the photochemical reactions of sulfate is stronger. As a result, the seasonal variation of sulfate concentrations is not evident. We will modify the statement in the revised manuscript.

"Particulate sulfate exhibits a relatively less pronounced seasonal pattern with a small peak in

June."

Lines 287-289: Writing is unclear. Is the NOx 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.

Response: Thanks for the comment.

Here, we want to explain the big discrepancy between the NOx and nitrate as shown in Fig.4. The NOx concentrations show a big drop. However, nitrate does not. This suggest that the nitrate we observed in February may be more associated with the regional issue/transport instead of local problem. The festival should be one of the reasons of the NOx decrease. Because during festival, people in college town (our site) usually come back to their hometown. As a result, local emissions will be significantly reduced. We will modify the description in the revised manuscript.

"The observations might suggest that particulate nitrate was influenced by regional transport but not the local emissions in February."

Line 290-299: The results of the equilibrium calculation do not make sense. HNO3 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 HNO3 above the line would be calculated to be in the aerosol phase. How was the calculation of HNO3 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.

Response: Thanks for the comment. We will remove the plot of equilibrium calculation in the revised manuscript.

The calculation we deployed in Fig. 5 considered only nitrate, ammonia and temperature. And the parameters of dissociation constant can be varied at different situations (Seinfeld and Pandis, 2006). This could the reason of the discrepancy. We agree with the referee's comment and will remove the

plot and related statement in the revised manuscript.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, John Wiley & Sons, New York, 2nd edition, 1232 pp., 13: 978-0-471-72018-8 2006.

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.

Response: Yes, thanks. We will replace Brown by Dube 2007 by Baasandorj et al. 2017 in the revised manuscript.

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?

Response: Yes, thanks. We mean that the influence of thermodynamics is smaller on the diurnal cycle in winter. We will modify the description in the revised manuscript.

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.

Response: Yes, it should be replaced by "percentile". Thanks for your reminder. We will correct the expression in the revised manuscript.

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?

Response: Thanks for the comment. The biomass burning activities occurred mostly from May 25 to June 10 instead of the whole summer (Ding et al., 2013). In Figure S3, the main biomass region is in the west and northwest of our site. In Fig.7 we can see that compared to the hours with bottom 25% nitrate concentrations, more air masses came from west and northwest during the hours with nitrate concentrations of top 25% percentile.

Ding, A. J., Fu, C. B., Yang, X. Q., Sun, J. N., Petäjä, T., Kerminen, V. M., Wang, T., Xie, Y.,

Herrmann, E., Zheng, L. F., Nie, W., Liu, Q., Wei, X. L., and Kulmala, M.: Intense atmospheric pollution modifies weather: a case of mixed biomass burning with fossil fuel combustion pollution in eastern China, Atmos. Chem. Phys., 13, 10545-10554, 10.5194/acp-13-10545-2013, 2013.

Line 432-433: The product of NO2*O3 is a proxy for the N2O5 production rate, but this could be calculated quantitatively in units such as molecules cm-3 s-1 or ppbv hr-1 quite easily by also multiplying by the NO2 + O3 rate constant. This would be more intuitive in Figure 10.

Response: Yes, it is more intuitive and better. Thanks for the comment. We will modify it in the revised manuscript.

Technical corrections:

Line 49: the Chinese government

Response: Thanks. We will correct it in the revised manuscript.

Line 68: the N2O5 concentration

Response: Thanks. We will correct it in the revised manuscript.

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

Response: Thanks. We will correct it in the revised manuscript.

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

Response: Thanks. We will correct it in the revised manuscript.

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

Response: Thanks. We will correct it in the revised manuscript.

Line 113: “of” in place of “on”

Response: Thanks. We will correct it in the revised manuscript.

Line 239: “ranges” instead of “range”

Response: Thanks. We will correct it in the revised manuscript.

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

Response: Thanks. We will correct it in the revised manuscript.

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

Response: Thanks. We will correct it in the revised manuscript.

Line 280: eliminate the word “commendably”

Response: Thanks. We will correct it in the revised manuscript.

Line 291: “calculate” rather than “calculated”

Response: Thanks. We will correct it in the revised manuscript.

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

Response: Thanks. We will correct it in the revised manuscript.

Line 316: “The equilibrium constant”

Response: Thanks. We will correct it in the revised manuscript.

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

Response: Thanks. We will correct it in the revised manuscript.

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

Response: Thanks. We will correct it in the revised manuscript.

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

Response: Thanks. We will correct it in the revised manuscript.

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

Response: Thanks. We will correct it in the revised manuscript.

Line 349: “product of NO2” rather than “production of NO2”. Also insert “the” before “production rate of nitric acid”

Response: Thanks. We will correct it in the revised manuscript.

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

Response: Thanks. We will correct it in the revised manuscript.

Line 399: the steady state approximation

Response: Thanks. We will correct it in the revised manuscript.

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

Response: Thanks. We will correct it in the revised manuscript.

Line 419: remove the word “has”

Response: Thanks. We will correct it in the revised manuscript.

Line 450: , and ammonium nitrate

Response: Thanks. We will correct it in the revised manuscript.

Line 453: contributed to the nitrate

Response: Thanks. We will correct it in the revised manuscript.

Line 457: the ISORROPIA II model

Response: Thanks. We will correct it in the revised manuscript.

Line 459: the biomass burning regions

Response: Thanks. We will correct it in the revised manuscript.

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

Response: Thanks. We will correct it in the revised manuscript.

Line 460: the North China Plain

Response: Thanks. We will correct it in the revised manuscript.

Line 466: replace “and” with “which”

Response: Thanks. We will correct it in the revised manuscript.

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

Response: Thanks. We will correct it in the revised manuscript.