Review comments for Zhang et al

This paper aims to investigate the formation and evolution of nitrate in clouds, which has been rarely studied, based on the size-resolved mixing state of nitrate in the individual cloud residual and cloud-free particles by single particle mass spectrometry and the mass concentrations of nitrate in the cloud water and PM2.5 in southern China. The data show the direct observational evidence for the enhanced nitrate formation in the cloud water and residual particles, which is attributed to the enhanced hydrolysis of N2O5. Such a comprehensive dataset is quite robust for discussions and conclusions. Given that the in-cloud process is critical to accurately evaluating the evolution and oxidative impacts of nitrate, which is increasingly important, the manuscript is worthy of publication after considering my suggestions.

We would like to thank the reviewer for his/her positive comments. We greatly appreciate the constructive suggestions, which are really critical to improve our manuscript. We have addressed the reviewer's concerns in the sections below and made the appropriate revisions to the manuscript, with reviewer's comments are in black text followed by our response in blue text. We believe that the manuscript has been substantially improved with the consideration of these comments.

Major Comments:

(1) The authors first exclude the scavenging of gas-phase HNO_3 as a major pathway through the analysis of the size distribution of nitrate RPA and RPA ratio (nitrate/sulfate). However, the discussions based on such data are not clear enough. More detailed comparison and/or theoretical basis should be included to support the discussion.

Thanks for your comment. We agree with the comment and thus we have further compared our result with that from a previous study, which indicates a predominant role of scavenging of gas-phase HNO_3. Their detailed analysis on the cloud processing of nitrate helps to support our discussion. The text has been revised to:

"As can be seen in Fig. 2, the RPA of nitrate and RPA ratios of nitrate to sulfate distributes relatively stable over the measured size range, which suggests that the gas phase scavenging of HNO_3 is not the dominant pathway in the present conditions. This is because gas-phase mass transfer would lead to enhanced nitrate in the smaller droplets with higher total surface area (Drewnick et al., 2007). Comparatively, the limited size dependence of nitrate for the cloud RES particles differs markedly from that observed by Hayden et al. (2008), showing a favorable presence of nitrate in smaller size, rather than sulfate in larger size. And their pattern could be well explained by the model calculation assuming that all of the cloud nitrate comes from the uptake of HNO_3. Therefore, our pattern at least indicates a limited contribution of gas-phase scavenging of HNO_3 to the observed nitrate in the cloud RES particles. As also discussed in the following section, the formation of HNO_3 would be certainly suppressed by the presence of cloud.". Please refer to Lines 231-243 of the revised manuscript.

(2) The authors show that the hydrolysis of N2O5 explains ~1-3% increase in the nitrate mass fraction in clouds, whereas the in-cloud processing contributed to > 5% increase, and two possible explanations were provided. I wonder if it is possible to reveal the most important factor and if there are other possibilities since the consideration of these explanations may still not fully explain the observation.

Thanks for your comment. It is first noted that we got the unit wrong when plotting the ozone concentration, and it has been revised in the new version. A recalculation show that nitrate (NO_3^-) from the hydrolysis of N_2O_5 represents ~5-15% of the measured nitrate (Fig. 3). It could roughly explain ~10% increase of the nitrate mass fraction in clouds (Fig. 1). We also indicate that there are some factors that may contribute to the uncertainties in the estimation. In addition to the two factors discussed in the original text, we further included the following text "In addition, the scavenging of HNO_3 may still contribute to the in-cloud nitrate production, as

estimated in section 3.3, although N_2O_5 hydrolysis still represents the dominant pathway.". Please refer to Line 297-310 of the revised manuscript.

(3) In Fig. S1, I noticed that the relative humidity is close to 100% during cloud events, but RH inevitably declines during the cloud-free period. Given that RH has a certain impact on the hydrolysis of N2O5 and the scavenging of gas-phase HNO3, which is worth to have some discussions on it.

We agree with the comment that RH has a certain impact on the hydrolysis of N_2O_5 and the scavenging of gas-phase HNO_3. In the present study, we focused on the in-cloud formation of nitrate. We compared the nitrate in cloud water and cloud residual particles collected during the higher RH (~100%) period (or cloud event) with fine particles collected during lower RH period (or cloud free conditions). The result clearly reflects the strong influence of cloud in the hydrolysis of N_2O_5, as discussed in section 3.1.

Through thinking about this comment, we realized that the influence of RH may also be reflected by the enhanced nitrate observed in the cloud INT particles, which were not activated as cloud droplets. Given that we have already discussed the enhanced nitrate in cloud droplets, we have only revised the manuscript to include the influence of RH in the formation of nitrate in the cloud INT particles as "The enhancement of nitrate in the cloud interstitial particles may also indicate that the significant role of RH in the formation of nitrate, even in the inactivated particles.". Please refer to Lines 250-252 of the revised manuscript.

Specific comments:

(1) Introduction: The authors summarized the previous studies on the in-cloud processing of nitrate and showed that the detailed observational investigations and the possible mechanisms governing nitrate behavior upon in-cloud processes are scarce. It would be better to include how these studies quantify the relative roles of each pathway for the formation of nitrate in clouds.

Thanks for the comment. Generally, models are applied to quantify the relative roles of each pathway for the formation of nitrate. As summarized, although the formation pathways of nitrates in aerosols have been relatively clear, the pathways and controlling factors for the formation of nitrates in clouds are still very scarce. To make it clear, we have included such description in the main text as "Therefore, more detailed information on the pathways of nitrate and controlling factors in cloud are still required for models to further integrate the role of cloud in the formation of nitrate in the troposphere (Zhu et al., 2020; Wu et al., 2021).". Please refer to Lines 86-89 of the revised manuscript.

(2) Line 141: The predefined sampling cloud droplet size is 7.5-8.5 μm. So why is the mean droplet size assumed to be at 7 μm when calculating the SA?

Thanks for your comment. As we noted in the manuscript, the estimated SA based on the arbitrarily selected mean droplet size should linearly correlate with real values and thus would not lead to ambiguous conclusions. For consistency, we have revised this value to 8 μm, which is also located in the typically reported ranges of the mean droplet sizes.

(3) Line 284: More detailed discussion should be provided to indicate the fast heterogeneous uptake coefficient, and also the specific values.

We agree with the comment. We have extended the discussion to indicate the fast heterogeneous uptake of N_2O_5 in highly humid condition, and to include the specific values. The sentence has been revised to "As previously reported, high aerosol LWC (campaign average at ~50 μg m^{-3}) induced fast heterogeneous uptake of N_2O_5 (γ = 0.048 on average) is prevalent in urban haze (Wang et al., 2017), compared with γ < 0.03 for normal periods, and thus results in enhanced nitrate in highly humid condition (Neuman et al., 2003; Wang et al., 2009; Pathak et al., 2009)."

(4) Line 356: The involvements of VOCs may impact the formation of nitrate through various mechanisms, e.g., direct reaction with NO3 or consumption the oxidants such as OH, which should be discussed in detail.

We agree with the comment that the involvements of VOCs may impact the formation of nitrate. However, the detailed mechanisms are still unclear and not included in the aqueous phase models yet. The most influential factor may be the direct reaction of VOCs with NO_3 radical. To make it clear, we have revised the sentences to "Note that biogenic volatile organic compounds could also have a potentially important impact on nitrate formation through reacting with NO_3 radical, which may lead to up to 35% decrease of particulate nitrate (Fry et al., 2014; Aksoyoglu et al., 2017)."

Figure 3: It will be easier to understand if the chemical formulas N2O5 and NO3- are written in the axes of the figure instead of "nitrate".

Thanks for your comment. We have revised the Figure as suggested.

SI line 47: It should be "Text S1".

Thanks for your comment. It has been revised as suggested.

SI figure S4: It's difficult to understand this figure, can you describe the horizontal and vertical coordinates more clearly in the figure caption?

Thanks for your comment. More information has been included to make it clear. The sentences "The RPA of nitrate, as an indicative of the relative abundance of nitrate in the individual particles, was presented in hourly average values. Such distribution shows that the cloud RES particles were associated with higher relative abundance of nitrate, rather than the cloud free particles." have been included in the Figure caption.

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