Response to comments

Comment from Referee #1:

General Comments: 1. The introduction (starting around line 77) is improved, but the reader would still benefit from a brief, referenced paragraph that discusses the link between particle size and cloud droplet size for a given chemical composition. I think this will really help lead into the discussion of enrichment. It is not abundantly clear to the reader is the Twohy 1989 result is that small particle grow to small droplets and large particles grow to large droplets, independent of composition, or if the connection to small droplets is via $(NH_4)_2SO_4$ and to large droplets through NaCl. This is the foundation of the manuscript and could be made much more clear. Essentially, this should be a concise introduction to the physics behind how chemical enrichment in large (or small) cloud droplets could come about.

Reply: We would like to thank the reviewer for his/her useful comments and recommendations to improve the manuscript. We had made careful revision according to the suggestions, please refer to the following responses for details.

Twohy et al. (1989) observed that small ammonium sulfate particles grew to small droplets and large sea salt particles grew to large droplets. Previous observations also considered that the supermicron or giant sea salt-containing particles readily became large cloud droplets, and their CCN behavior was less affected by chemical composition (Noone et al., 1988; Monger et al., 1989; Andreae and Rosenfeld, 2008; Tao et al., 2012). So far, the study on the submicron sea salt-containing particles in cloud droplets is scarce in the literature. Additionally, the existence of secondary species (e.g., sulfate, nitrate, or organic species) onto the submicron sea salt-containing particles might significantly impact on their cloud activation (O'Dowd et al., 1999; Gibson et al., 2006; Nguyen et al., 2017). Please refer to Lines 79-88 in the modified manuscript.

2. I think it would be tremendously helpful to have a figure (comparable to figure 3A, but for particles) that shows the number fraction of sea-spray (or sea-salt as termed here) as a function of particle size for the ambient aerosol (not cloud residuals). This

distribution could then be compared to the cloud residual distribution to identify enrichment. The paper currently argues that compositional differences in submicron SSA drive the observed changes in the cloud residual number fractions. This may be true, but more detail on the ambient aerosol distribution would help support (or refute) this argument.

Reply: We had added the size distribution of sea salt particles during cloud-free periods (Figure S4). During cloud-free periods, sea salt particles accounted for 2% of the total ambient aerosol particles, and higher number fraction was observed in the supermicron particles (20%) than in the submicron particles (1%). Meanwhile, the submicron sea salt particles contained higher proportions of organic nitrogen (73-94% versus 58%, by number), hydrocarbon organic species (51-81% versus 2%) and organic acids (35-72% versus 4%) in the ambient aerosol particles than in the cloud residues at cut size of 7.5 μm. This further supports that the enhancement of organic species in the submicron particles likely reduced CCN activity of sea salt particles. Please refer to Lines 210-211, 292-293 and 363-368 in the modified manuscript and Figure S4 in the modified Supplement.

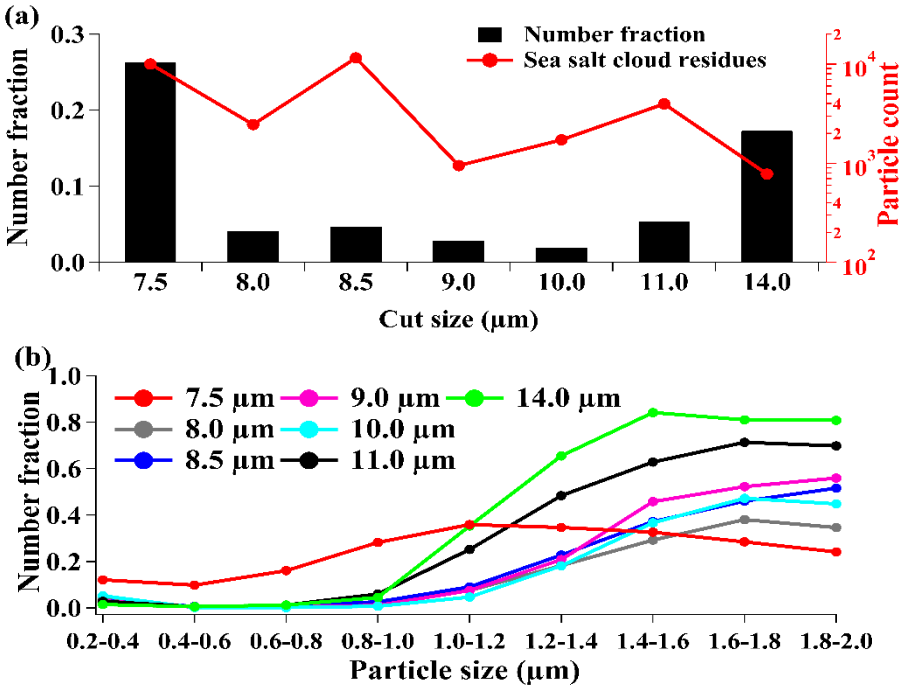

Figure 3. Number fraction or counts of sea salt-containing cloud residues as a function of the cut size (a) and the relative contribution of sea salt-containing cloud residues to the total cloud residues in the given size range (b).

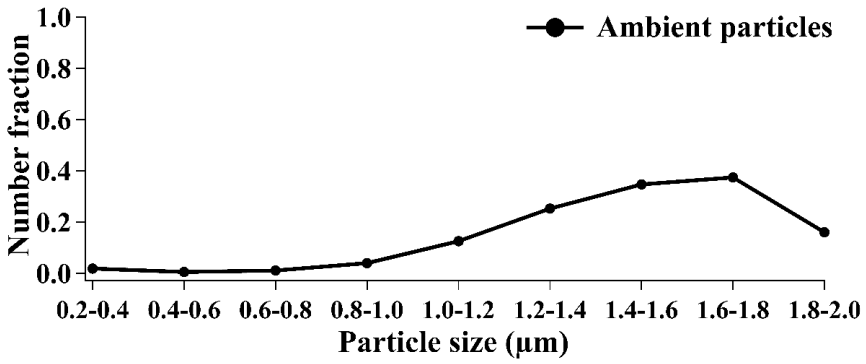

Figure S4. The relative contribution of sea salt-containing particles to the total particles in the given size range during cloud-free periods.

Specific Comments

Line 43: I don't think that Cochran et al is an appropriate primary reference for this statement.

Reply: The reference of Cochran et al. had been replaced by Boucher et al. (2013),

which summarized assessment report of the Intergovernmental Panel on Climate Change (IPCC). Please refer to Line 46 in the modified manuscript.

Line 52: I'm not sure how well founded this sentence is. The uncertainty in the CCN activity of sea-spray aerosol is much more a function of variance in the size distribution of SSA than its composition outside of the smallest SSA. There remain open questions as to why the hygroscopicity of SSA is so high given the organic content. See Collins et al., GRL 2016 (https://doi.org/10.1002/2016GL069922)

Reply: We agreed with the comment. Collins et al. (2016) found that large increases in the organic matter fraction of freshly emitted sea-spray aerosols only induce less than 3% change in CCN concentrations, and they also suggested that secondary aerosol chemistry may be the more important factor linking ocean biogeochemistry to marine clouds. In this study, we found that atmospheric ageing processes would alter chemical composition of sea salt particles, might thus influence CCN behavior. The sentence had been changed to "Therefore, it is important to evaluate the impact of chemical composition and particle size on the CCN behavior of sea salt particles." Please refer to Lines 53-55 in the modified manuscript.

Line 58: Given that SSA is largely organic, consider changing from sea salt aerosol to sea spray aerosol.

Reply: We had changed accordingly. Please refer to Line 59 in the modified manuscript.

Line 64: I don't think the conclusion of Wang et al 2015 is that the enrichment does not always occur. The conclusion is that the fraction of aliphatic organic material in SSA has some level of variability given surface ocean composition.

Reply: We had changed to "the fraction of organics (i.e., aliphatic organic material) in small sea spray aerosols exhibited some levels of variability in the similar simulation of ocean seawater conditions". Please refer to Lines 64-67 in the modified manuscript.

Figure 4 is extremely complicated. I would recommend a more detailed figure caption

that defines what “mixing fraction means”. Is one to interpret that a value of 1 (or red) for nitrate is that all of the particles detected at this size have nitrate?

Reply: The mixing fraction is defined as the number particles of a given compound divided by the total number particles. Yes, value of 1 (red color) for nitrate at the given cut size represented 100% of the total detected particles internally mixed with nitrate. Please refer to the caption of Figure 4 in the modified manuscript.

Response to comments

Comment from Referee #2:

This manuscript samples clouds from a mountain site in China using a ground counterflow virtual impactor (GCVI) and a single particle mass spectrometer. The authors used different cutsizes on the GCVI to look at different slices of the cloud droplet size distribution. They then identified only sea salt-containing cloud residues and compared the chemical mixing state of the sea salt particles across the different cloud droplet size cuts. I think this paper did a nice job of referencing relevant literature; however, I think more attention needs to be paid to the role of cloud processing on the chemical makeup of the cloud residues. I think this paper needs major revision before publication.

We would like to thank the reviewer for his/her useful comments and recommendations to improve the manuscript. We agree with the comments, and careful revision has been made according to the suggestions, please refer to the following responses for detail.

General Comments: What about cloud processing? You don't really discuss cloud processing and how this could affect your results or interpretation of the results. I think this is a mistake and you should think about how cloud formation and cloud processing will influence the size of the cloud droplets as well as the chemical makeup of the cloud residues.

Reply: We agree with the comment. Both cloud formation and cloud processing would alter size and chemical composition of the cloud droplets. Relative to small cloud droplets, larger cloud droplets might undergo longer duration cloud (Nakajima et al., 2010), thus increase the in-cloud formation of secondary species. From this study, higher number fraction of sulfate, ammonium, and organic species (e.g., oxalate) in the sea salt-containing cloud residues at the cut sizes of 8-14 μm was compared to the cut size of 7.5 μm. This might be due to the larger cloud droplets having longer duration cloud, leading to the increase of these secondary species. Please refer to Lines 246-249, 304-307 and 350-354 in the modified manuscript.

How quickly was the cutsize changed on the GCVI? What were the sampling time periods for each cutsize?

Reply: The cloud droplet cut sizes and duration time set in the GCVI system are presented in Table S1. The minimum sampling time for each cut size was 12 hours. Please refer to Lines 122-124 in the modified manuscript and Table S1 in the modified Supplement.

Table S1. The time for the seven cut sizes set in the GCVI system.

Cut sizes	Start time	End time	Duration (Hour)
7.5 μm	20.05.2017, 21:00	21.05.2017, 14:00	17
8.0 μm	24.05.2017, 14:00	24.05.2017, 20:00	06
8.0 μm	25.05.2017, 01:00	25.05.2017, 12:00	11
8.0 μm	26.05.2017, 00:00	26.05.2017, 05:00	05
8.5 μm	22.05.2017, 19:00	23.05.2017, 07:00	12
8.5 μm	30.05.2017, 02:00	30.05.2017, 08:00	06
8.5 μm	30.05.2017, 19:00	02.06.2017, 21:00	50
9.0 μm	02.06.2017, 21:00	03.06.2017, 14:00	17
10.0 μm	23.05.2017, 08:00	24.05.2017, 00:00	16
11.0 μm	08.06.2017, 01:00	08.06.2017, 08:00	07
11.0 μm	08.06.2017, 18:00	10.06.2017, 17:00	47
11.0 μm	10.06.2017, 19:00	11.06.2017, 08:00	13
14.0 μm	04.06.2017, 12:00	05.06.2017, 12:00	24

What is the lowest size cut that the GCVI can reliably produce? Was the data for the lowest size cut given in the paper so different from the rest because there was a more breakthrough at the lower size cut? Did you see more supermicron particles at the lower size cut?

Reply: The lowest cut size of the GCVI was set to be 7.5 μm in this work. Yes, higher number fraction of supermicron cloud residues have been found at the lowest size cut

of 7.5 μm (50%) as well as at the maximum size cut of 14 μm (23%) relative to the other cut sizes of 8.0-11.0 μm (9-19%). Pekour and Cziczo (2011) observed that the breakthrough of large particles tended to increase at the lower size cut. In this study, the number concentration of ambient particles in the GCVI downstream inlet was below 1 cm^3 at the lowest cut sizes during cloud-free periods, hence the large particle breakthrough at the lowest cut size seemed to be quite low. Please refer to Lines 130-134 in the modified manuscript.

Specific Comments:

Lines 18-19: "The effect of size-resolved sea salt-containing particles on cloud condensation nuclei (CCN) is incompletely understood." This sentence doesn't make sense. I would remove "size-resolved" or specify more clearly that sea salt particles of different sizes have different chemical compositions and thus different CCN activities.

Reply: We thank the reviewer for this suggestion. We have changed to "The effects of chemical composition and size of sea salt-containing particles on their cloud condensation nuclei (CCN) activity are incompletely understood". Please refer to Lines 19-20 in the modified manuscript.

Lines 29-32: This sentence is confusing as written. I would rewrite to say that nitrate was internally mixed with over 90% of particles and continue this phrasing with the rest of the compounds listed.

Reply: We have modified accordingly. Please refer to Lines 31-32, 34-36, 227-232, 256-257, 297-300, 304-307, 323-326, 340-341 and 376-378 in the modified manuscript.

Lines 32-35: Same comment as above. Rephrase to state these compounds are internally mixed with X% of particles.

Reply: We have modified accordingly. Please refer to Lines 34-36 in the modified manuscript.

Lines 40-43: "The observed findings of this study highlight the enrichment of

submicron sea salt-containing particles in small cloud droplets, which would induce decreased precipitation and, in turn, affect their residence time in the atmosphere." Why would the presence of sea salt in clouds decrease precipitation? Are the concentrations so great that the cloud droplets do not grow large enough to precipitate?

Reply: Our result showed that the submicron sea salt-containing particles can enrich in small cloud droplet. Thus they might need longer time to grow large enough to precipitate (Tao et al., 2012). Oppositely, the supermicron sea salt-containing particles readily become large cloud droplet, possibly leading to accelerate the conversation of cloud droplet to precipitation (Tao et al., 2012). We have clarified them: "This study provided a significant contribution towards a comprehensive understanding of sea salt CCN activity". Please refer to Lines 39-41 in the modified manuscript.

Increase in concentration of submicron sea salt-containing nuclei probably slow the conversion of cloud drops into precipitation due to the competition of water vapor among cloud drops (Tao et al., 2012). Unfortunately, the number concentration of sea salt-containing particles within cloud droplet cannot be obtained by the instrument used in this study.

Line 69: Aged should be aging.

Reply: We have modified accordingly. Please refer to Line 68 in the modified manuscript.

Lines 94-96: I don't understand this sentence. Why would the cloud droplet size dictate or correlate to the sea salt size?

Reply: We have change to "Twohy et al. (1989) observed that small ammonium sulfate particles grew to small droplets and large sea salt particles grew to large droplets. Previous observations also considered that the supermicron or giant sea salt-containing particles readily became large cloud droplets, and their CCN behavior was less affected by chemical composition (Noone et al., 1988; Monger et al., 1989; Andreae and Rosenfeld, 2008; Tao et al., 2012). So far, the study on the submicron sea salt-containing particles in cloud droplets is scarce in the literature. Additionally, the

existence of secondary species (e.g., sulfate, nitrate, or organic species) onto the submicron sea salt-containing particles might significantly impact on their cloud activation (O'Dowd et al., 1999; Gibson et al., 2006; Nguyen et al., 2017)". Please refer to Lines 79-88 in the modified manuscript.

Line 145: SPAMS is misspelled.

Reply: We have changed "SAPMS" to "SPAMS". Please refer to Line 141 in the modified manuscript.

Line 220-221: "In contrast to these findings, our results reflect that sea salt-containing nuclei are insensitive to the increase in the cloud droplet size." But you just stated that the number fraction of sea salt particles changed with different GCVI cut sizes. Please explain what you mean.

Reply: Lines 220-221 have been changed to "In contrast to these findings, the maximum number fraction of sea salt-containing cloud residues was found in the minimum GCVI cut size". Please refer to Lines 217-219 in the modified manuscript.

Lines 246-249: "together with the enrichment of sea salt-containing cloud residues for the minimum cut size of 7.5 μm that was observed here, this might indicate that the distribution of sea salt-containing cloud residues that were dependent on cloud droplet size is likely influenced by changes in the chemical mixtures of sea salt-containing nuclei." What about cloud processing? Couldn't it be that the smallest cloud droplets are the youngest and thus had less time to undergo cloud processing? That could be why there is a smaller amount of secondary species observed in the smaller cloud droplets. Also, how quickly were you switching between the different cut sizes? Where the different cutsizes measured on the same day or different days? This could affect the results.

Reply: We agree with the comment. The smallest cloud droplets encountering less time of cloud processing probably reduce the in-cloud formation of secondary species. We have emphasized that lower number fraction of sulfate, ammonium, and organic species

(e.g., oxalate) in the sea salt-containing cloud residues for the cut size of 7.5 μm was compared to the cut sizes of 8-14 μm, likely due to the smallest cloud droplets having shorter duration cloud, leading to the decrease of these secondary species. As listed in Table S1, the particles with different cut sizes were measured in the different days, so the sea salt-containing particles might undergo different atmospherically aging processes or transport routes (Figure S2). Therefore, less aging processes during atmospheric transport might be another contributor to the smaller amount of secondary species in the lowest cloud droplet cut size. Please refer to Lines 246-249, 304-307 and 350-354 in the modified manuscript, Table S1 and Figure S2 in the modified Supplement.

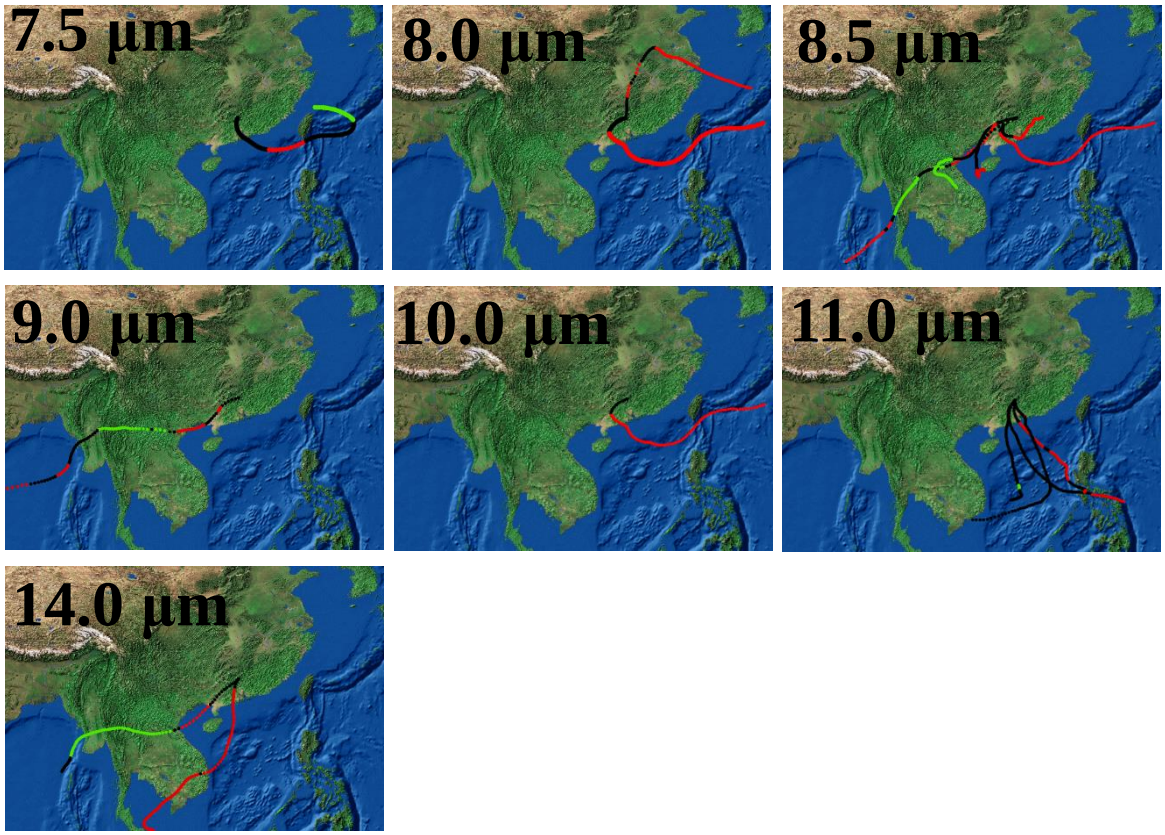

Figure S2. The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) back trajectories (96 h) for air masses at 1800 m (above sea level) during cloudy events. The red, black, and green colors represent the transport heights of 0-1 km (above sea level), 1-2 km, and above 2 km, respectively.

Lines 295-305: No. This implies that the nitrogen could be integrated into the particles during atmospheric transport and the sulfate and ammonium are likely introduced by cloud processing, thus why they are present in the larger cloud droplets.

Reply: We agree with the comment. Nitrate internally mixed with over 90% of the sea salt-containing cloud residues with different cut sizes was more likely due to the aging processes during atmospheric transport, rather than the in-cloud formation. As mentioned above, the variation in sulfate and ammonium of sea salt-containing cloud residues with different cut sizes might be affected by both in-cloud formation and aging processes during atmospheric transport. Higher number fraction of sulfate and ammonium in the larger cloud droplets likely have longer duration cloud or more aging processes during atmospheric transport. Further study needs to compare the contribution of duration time of cloud process or aging degree to the content of secondary species. Please refer to Lines 246-251 in the modified manuscript.

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