

Response to comments

Manuscript Number: acp-2017-23

Title: In situ chemical measurement of individual cloud residue particles at a mountain site, South China. Qinhao Lin et al.

Summary and general comments

The authors present the results of online physico-chemical characterization of cloud residuals ($> \sim 8 \mu\text{m}$ in diameter), cloud particles ($< 2.5 \mu\text{m}$ da) and ambient particles ($< 2.5 \mu\text{m}$ da) from the field study conducted in January, 2016 in a remote mountainous area of South China. Based on the dataset of the eight major particle types classified by using the SPAMS data obtained during several cloud events, the authors report some unique properties of cloud residuals, such as chemical composition, size and mixing state (that may be inherently related), presumably occurred during an aerosol's atmospheric aging and cloud processes.

The topic itself is an important addition to ACP. Overall, the authors conducted a careful study as well as rigorous data analyses to generate new results regarding cloud residuals that would be potentially valuable in the cloud microphysics research community. However, such care was unfortunately not taken in the preparation of the manuscript, with the manuscript containing a number of errors and typos. Although I do not have any major scientific concerns, I have numerous technical comments (including but not limited to) as listed below. I would urge the authors of the manuscript to thoroughly proof read their manuscript as this list gets too long.

[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.](#)

Specific comments

P4 L64-P5L78: This part is not well written and poorly structured. The authors need to logically address why it is particularly important to study the aerosol mixing state rather than just focus on other general properties, such as size (e.g., Dusek et al., 2006, Science; Sotiropoulou et al 2006, Aerosol Science & Technology) and bulk composition (e.g., Wiedensohler et al., 2009, JGR; Twohy and Anderson, 2008, Environmental Research Letters), to improve our understanding of CCN activation. Aerosol mixing state indeed influences the ability of aerosol to act as CCN (e.g., Wang et al., 2010, Aerosol Science & Technology). For instance, Medina et al. (2007, JGR) estimated that internal mixing assumption resulted in a 35% over prediction of CCN concentration in one study for semi-urban settings. However, the relative importance of the mixing state as compared to other properties appear to vary depending on the proximity to the pollution plume source and/or photochemical ageing activity as a function of oxidant concentrations (Ervens et al., 2010, ACP). Hence, additional detailed measurements to characterize the timescale and effect of the aerosol mixing state on CCN properties of particles are by all means needed to improve our theoretical understanding of CCN

activation. Please do not copy and paste the reviewer's comments in the manuscript. The authors may want to do a careful and thorough literature review, digest the contents in a diplomatic manner and describe your thoughts to the reader along with your own story line. I also suggest the authors to address up-to-date information of lab studies regarding the effect of the aerosol mixing state on CCN ability or droplet activation (e.g., Wang et al., 2017, ACPD-2017-454 and references therein; Broekhuizen et al., 2004, GRL; Abbatt et al., 2005, Atmospheric Environment; Shilling et al., 2007, Journal of Physical Chemistry A). Explaining how your field study would potentially shed light on lab works, vice versa, may strengthen the paper.

The part has been restructured. The ability of aerosol particles to act as cloud condensation nuclei (CCN) is dependent on the size and chemical composition of atmospheric aerosol particles at a given supersaturation (McFiggans et al., 2006). Wiedensohler et al. (2009) found that the enhancement of particles CCN ability was related to an increase in the average sulfate mass concentration. Dusek et al. (2006) demonstrated that CCN behavior was more effected by aerosol size than chemical composition. Meanwhile, aerosol mixing state also play an important role in the ability of aerosol to act as CCN. It has been reported that freshly emitted elemental carbon (EC) particles generally exhibit low CCN activity, whereas aged EC particles show high CCN activity after experienced atmospheric processes (Zhang et al., 2008). Pratt et al. (2011) found that number fractions of ammonium or oxalate internally mixed with biomass burning particles increased with an aged time of 81-88 min, which promote CCN behavior. Laboratory studies have shown that low-solubility organic particles internally mixed with ammonium sulfate would suppress water uptake of mixed particle and thus might affect CCN activity (Wise et al., 2003; Svenningsson et al., 2006; Sjogren et al., 2007). An over prediction of CCN concentration by up to 35% was estimated based on particle internal mixing state assumption (Medina et al., 2007; Collins et al., 2013). The influence of mixing state on aerosol CCN activity varies depending on the proximity to the pollution plume source and/or photochemical ageing activity (Ervens and Volkamer, 2010). More detailed measurements to characterize the mixing state of CCN particles would improve our understanding of aerosol-cloud interactions. Our result was compared with previous lab measurements (McMeeking et al., 2011; Tang et al., 2016). Please refer to Lines 64-83, 356-358 and 375-378 of the revised manuscript.

P7L125-126: The authors state that the observed clouds contained only liquid droplets. This statement is speculative since the ambient temperature seemed to be below -7 °C at some point of the field campaign (P7L125), which could trigger heterogeneous ice nucleation of some materials contained in dust aerosols (e.g., Atkinson et al., 2013, Nature). Further scientific backing seems necessary for the reader to understand the cloud properties.

Only 20 cloud residues that accounted for 0.08% of the total cloud residues were detected when the ambient temperature was below -7 °C observed from 06:00 to 08:00

on 23 Jan. Thus, cloud droplets were dominated by liquid water droplets. Please refer to Lines 130-133 of the revised manuscript.

P7 L126-128: Was the ambient inlet coupled with a dryer downstream? Please clarify.

The ambient inlet was dried using a diffusion dryer. Please refer to Lines 148-149 of the revised manuscript.

P7L130-131: “Therefore, it is reasonable to select...” - I disagree with this statement. Correctly, the authors presumed the droplet size to be larger than 8 μm . This assumption should be stated in the manuscript.

“Therefore, it is reasonable to select...” assuming that size distribution of cloud droplet mostly was above 8 μm in this region”. Please refer to Lines 137-138 of the revised manuscript.

P7L130-131: There have been observations of droplet size-dependent chemical composition in clouds (Moore et al., 2004, Atmospheric Environment). Please discuss it in the manuscript.

We have added the reference as “Previous measurements have found that dust, playa salts, sea salt or metal particles were often enriched in larger cloud droplets ($\sim 20 \mu\text{m}$) (Bator and Collett, 1997; Moore et al., 2004; Pratt et al., 2010b).”. Please refer to Lines 341-343 of the revised manuscript.

P7131-134: What gas (i.e., dry synthetic air, nitrogen, etc.) was used to create the counterflow? What is the background aerosol concentration through GCVI (i.e., the measurement with the counterflow only) in this study? In addition, can the authors at least provide the estimate of the number fraction of residuals to total particles relevant to your study (i.e., CCN active fraction)? Did the author measure the total cloud particle concentration through GCVI without any counterflows at some point?

A stream of filtered and heated ambient air (counterflow) was provided by a compressor. During cloud-free periods, a ratio of concentration (below 1 cm^{-3}) behind the CVI to background aerosol concentration ($2,000 \text{ cm}^{-3}$) was 0.0005, indicating that instances of particle breakthrough and small particle contamination were absent. A ratio of number residuals to total number particles (sum of cloud residues and non-activated particle) on average was 0.43 ± 0.20 , when cloud residues and non-activated particles were alternately sampled with an interval of one hour during the cloud III event. We have not measured the total cloud particle concentration through GCVI without any counterflows. Please refer to Lines 141-142, 149-152 and 179-182 of the revised manuscript.

The particle transmission efficiency of residual sampling instruments is size-dependent.

Did the authors take it into account for your analyses or apply 50% loss throughout the analyses? Please clarify. It is not clear if the size-dependence is incorporated in your analyses (P11L225-228). Just citing a paper seems not enough to justify it.

We have discussed effect of particle transmission efficiency of the SPAMS and GCVI on change in number fractions of cloud residual types. Dust residues may have occupied larger CCN (Tang et al., 2016) and OC particles existed in smaller cloud residues (Sellegri et al., 2003a), which cannot be detected by the SPAMS. This might lead to underestimate fractions of these particle types due to the limitation of the SPAMS. Moreover, the particle transmission efficiency of the GCVI increased with increasing cloud droplet size (Shingler et al., 2012), might leading to relatively larger fractions of the large cloud droplets. Please refer to Lines 303-304, 332-334 and 345-348 of the revised manuscript.

P7L139: Why do the authors define what comes through an ambient inlet (2.5 micron 50% cut-off) as "non-activated" particles? Numerous lab and field studies show that submicron particles can be activated to <2.5 micron.

It is assumed that the mean diameter of cloud droplets was around 8 μm . It is possible that cloud droplet could have size < 2.5 μm . It is hard to define a critical fog/cloud droplet diameter that is highly variable (ranging from 1 to 5 μm) (Hammer et al., 2014). The "non-activated" (interstitial) particles inlet has a cutoff of 2.5 μm in previous work (Verheggen et al., 2007). Therefore, a similar cutoff was used to sample non-activated particles during the cloud events. Please refer to Lines 137-138 and 147-148 of the revised manuscript.

P9L165-166: What about the transmission efficiency? Was it accounted, too? Please clarify.

The measured cloud residual concentration was integrated by a SMPS and was then corrected by the enrichment factor and transmission efficiency of the GCVI. Please refer to Line 177 of the revised manuscript.

P10L197: cloud formation \rightarrow high RH condition. Unless the authors provide the data of cloud properties, it is not fair to say cloud formation.

We agree with comment and have corrected accordingly. Please refer to Line 214 of the revised manuscript.

P12L244-246: The local biomass burning also contributes to the aerosol-cloud interaction in the North Slope of Alaska (Hiranuma et al., 2013, JGR), which seems more relevant to your study.

We have added the reference and have discussed contribution of local biomass burning

to the aerosol-cloud interaction in the North Slope of Alaska. Please refer to Lines 263-264 of the revised manuscript.

P13L257-259: So how did this 266 nm enrichment influence your own results? Please clarify.

Amine peak areas would be enhanced when using a 266 nm ionization laser and amines themselves may not comprise the majority of the particle mass (Pratt et al., 2009). The SPAMS only provide a qualitative information and is not directly related to particle mass. Therefore, the sentence has been detected in the revised manuscript.

P13L263-267: So what determines the ambient abundance of amines in this particular study? Please be conclusive.

Presence of gas-phase amine sources determines the ambient abundance of amines. The potential gas amine emissions from ocean and livestock areas might promote the enrichment of amine particles in this study. Please refer to Lines 284-287 and 456-459 of the revised manuscript.

P13L268-269: What is the implication of Bi et al. with respect to your study? Please be conclusive.

It might suggests that enhancement of particle amine is not only depend on high RH or fog/cloud process, but also sensitive to other parameters, such as presence of gas phase amine source (Rehbein et al., 2011). Please refer to Lines 284-287 of the revised manuscript.

P14L286-287: The authors may state that a low fraction of dust is the limitation/artifact.

We agree with comment and have corrected accordingly as “Hence, a low fraction (2.9% by number) of dust cloud residue might be due to the limitation of the SPAMS.” Please refer to Lines 303-304 of the revised manuscript.

P14L288-296: Moteki et al. (2017, Nature Comm.) reports the aircraft observation of magnetite (up to $\sim 1 \text{ cm}^{-3}$) over the East Asia. The authors may read, digest and incorporate it in your manuscript.

We have cited the reference. The contribution of anthropogenic and natural Fe-containing particles sources (Moteki et al., 2017) to observed Fe-containing residues is discussed. Please refer to Lines 310-311 of the revised manuscript.

P14L299-P15L310: Was a depletion of chloride (e.g., Laskin et al., 2012, JGR) dominant in this study?

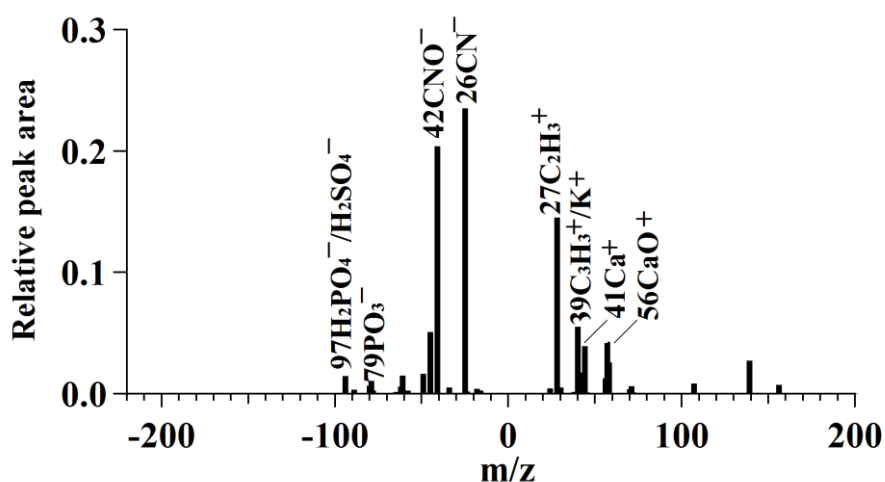
The acid displacement reactions of sea salt chloride with HNO₃ during atmospheric aged process might lead to a depletion of chloride (37%) and a high fraction (89%) of nitrate in the Na-rich residues. Please refer to Lines 354-356 of the revised manuscript.

P15L308-309: Can the authors quantitatively differentiate the source (industrial vs. maritime) by looking at other types of particles came along with the Na-rich particles?

The number fraction of the Na-rich cloud residues did not increase from continental (Northerly) air mass on 19 Jan to maritime (southwesterly) air mass on 21 Jan (3.3% versus 2.4% by number). It limits the analysis to quantitatively differentiate other types of particles came along with the Na-rich particles. Instead, a comparison of related sea salt ion peak area was performed for the Na-rich residues at varied air masses. Please refer to Lines 319-323 of the revised manuscript.

P15L311-319: Just for curiosity, did the authors find any biological particles during the campaign? If so, how many of those are classified as Other?

Only three particles in the Other type were found to contain calcium, organic carbon, organic nitrogen and phosphate ion signals, suggesting existence of biological particles (Pratt et al., 2009a). Please refer to Lines 337-340 of the revised manuscript.



P17L353-354: In P16L338-340, the authors state that the ammonium nitrate is not a dominant form of nitrate in this study, which seems contradicting to the statement given here...

Relative to nitrate, low portions of ammonium (m/z, 18NH₄⁺) in the Na-rich (23% by number) and Dust (15% by number) cloud residues suggest that in this region, ammonium nitrate was not a predominant form of nitrate in the Na-rich and Dust cloud residues. High portions (75-86% by number) of ammonium-containing particles were

observed for the OC and aged EC cloud residues. This result implies that ammonium-containing particles are preferentially activated or enhanced by uptake of gaseous NH_3 to neutralize acidic cloud droplets for the OC and EC types. Please refer to Lines 362-364 and 378-381 of the revised manuscript.

P17L360-361: What is the measurement uncertainty regarding TMA counts?

The TMA accounted for up to 93% by number of the Amine cloud residues. Please refer to Line 386 and Figure 5 of the revised manuscript.

P21L457-458: So size or mixing state-which factor was determinant to determine the cloud formation ability in this particular period?

The enhancement on number fraction or intensity of nitrate-containing cloud residues was not observed when compared with non-activated particles during this particular period. On the contrary, a large size distribution of nitrate-containing cloud residues (Figure S7) was found when compared with non-activated particles. This result reflects that particle size, rather than mixing state/nitrate content, plays a more important role in the activation of particles into cloud droplets during this particular period. Please refer to Lines 515-519 of the revised manuscript.

Technical comments

P3L45 & P4L57: Be consistent with 'in situ' or 'in-situ'.

We have corrected accordingly. Please refer to Line 47 and 57 of the revised manuscript.

P4L56: →...and, in turn, affect...

We have corrected accordingly. Please refer to Line 56 of the revised manuscript.

P4L59: Although → Despite or Even with

We have corrected accordingly. Please refer to Line 60 of the revised manuscript.

P4L64: The formation of → The ability of aerosols to act as

We have corrected accordingly. Please refer to Line 64 of the revised manuscript.

P4L71: Too many 'however's are bothering. There are a total of 10 however-sentences appearing in this manuscript.

We have detected some 'however's in the revised manuscript.

P5L79: → an Aerosol Mass Spectrometer (AMS) or other online/offline single particle instruments is

We have corrected accordingly. Please refer to Lines 84-85 of the revised manuscript.

P5L87: Oceans sound awkward.

We have changed “Oceans” to “marine areas”. Please refer to Line 93 of the revised manuscript.

P5L88: Start a new paragraph.

We have corrected accordingly. Please refer to Line 95 of the revised manuscript.

P5L90-93: → Although scientists have worked to...in China (Zhang et al., 2012b), only few studies have employed...

We have corrected accordingly. Please refer to Lines 96-99 of the revised manuscript.

P5L94: → obtain the mixing state of individual ambient particles during

We have corrected accordingly. Please refer to Lines 100-101 of the revised manuscript.

P5L95: → Their results showed...large particles

We have corrected accordingly. Please refer to Lines 101-102 of the revised manuscript.

P6L98: → fog residual particles at ground level in an urban area of South China.

We have corrected accordingly. Please refer to Line 105 of the revised manuscript.

P6L99: → They found an abundance of anthropogenic particles, including...

We have corrected accordingly. Please refer to Line 106 of the revised manuscript.

P6L102: → a mountain site in South China

We have corrected accordingly. Please refer to Line 108 of the revised manuscript.

P6L113: → Our measurements were carried out during...

We have corrected accordingly. Please refer to Line 118 of the revised manuscript.

P6L115: → This station is located at 200 km...

We have corrected accordingly. Please refer to Lines 120-121 of the revised manuscript.

P6L117: → ...(273 km²), where...

We have corrected accordingly. Please refer to Lines 122-123 of the revised manuscript.

P7L124: →The ambient temperature

We have corrected accordingly. Please refer to Line 129 of the revised manuscript.

P7L126: → The measurements of the droplet size spectra in this region performed during the winter of..

We have corrected accordingly. Please refer to Lines 133-134 of the revised manuscript.

P7L129: Some → Previous

We have corrected accordingly. Please refer to Line 136 of the revised manuscript.

P8L151: each singe → single (or individual particles)

We have corrected accordingly. Please refer to Line 162 of the revised manuscript.

P9 170-171: Providing references for these two sentences would be nice.

We have added a reference (Bi et al., 2016). Please refer to Line 186 of the revised manuscript.

P9L169-170: → Low levels of...exclude

We have corrected accordingly. Please refer to Line 183 of the revised manuscript.

P9L175: 73,996 →be consistent with the use of "," to describe numbers throughout the manuscript.

We have corrected accordingly. Please refer to Lines 190-192 of the revised manuscript.

P9L180: → similar clusters, such as aged EC, ...

We have corrected accordingly. Please refer to Lines 195-196 of the revised manuscript.

P9L184: → Assuming that the number of...

We have corrected accordingly. Please refer to Line 199 of the revised manuscript.

P10L198-199: I suggest deleting two 'and's

We have corrected accordingly. Please refer to Lines 213-215 of the revised manuscript.

P10L200: → Note that, on...

We have corrected accordingly. Please refer to Line 216 of the revised manuscript.

P11L211: The word "big freeze" is a nomenclature that may refer to something else. I suggest rewording it.

"big freeze" has been modified to "cold wave". Please refer to Line 227 of the revised manuscript.

P11L216: → the main six particle types

We have corrected accordingly. Please refer to Lines 232-233 of the revised manuscript.

P11L221: → The strong K⁺ ion...

We have corrected accordingly. Please refer to Line 237 of the revised manuscript.

P11L221-222: Awkward/incomplete sentence - I suggest rephrasing the sentence.

We have changed to "The strong K⁺ ion signal in the aged EC particles implies partially originated from biomass burning sources." Please refer to Lines 237-238 of the revised manuscript.

P11L227: → suffer from the bias related to...

We have corrected accordingly. Please refer to Lines 243-244 of the revised manuscript.

P11L232: → ...(m/z -46NO₂⁻, -62NO₃⁻) and presumably derived from...

We have corrected accordingly. Please refer to Line 249 of the revised manuscript.

P12L234: → An aged time of 81-88 min...showed an increase...

We have corrected accordingly. Please refer to Lines 250-251 of the revised manuscript.

P12L246: → the majority of aged EC

We have corrected accordingly. Please refer to Line 264 of the revised manuscript.

P12L246: → Asian

We have corrected accordingly. Please refer to Line 263 of the revised manuscript.

P12L249-250: → ...particles were only...droplets, and the aged EC residuals were...

We have corrected accordingly. Please refer to Lines 268-269 of the revised manuscript.

P12L251-252: → The Jungrauoch station is predominantly within the free tropospheric condition, such that the biomass...

We have corrected accordingly. Please refer to Lines 269-271 of the revised manuscript.

P13L262: → the size range

We have corrected accordingly. Please refer to Line 278 of the revised manuscript.

P13L263: → Aqueous reactions improving ... have been observed...

We have corrected accordingly. Please refer to Lines 279-280 of the revised manuscript.

P13L267: → ...amine within the cloud.

We have corrected accordingly. Please refer to Lines 283-284 of the revised manuscript.

P13L273: → Previous studies showed that dust particles that are internally mixed with sulfate and nitrate promote CCN activities...

We have corrected accordingly. Please refer to Lines 289-290 of the revised manuscript.

P13L275: partly → partial

We have corrected accordingly. Please refer to Line 291 of the revised manuscript.

P13L276: A slightly increase → A slight increase

We have corrected accordingly. Please refer to Line 293 of the revised manuscript.

P13L273: Internal mixing ... is expect to act as CCN... → Dust particles that are

internally mixed with sulfate and nitrate are expected to act as CCN...

We have corrected accordingly. Please refer to Lines 289-290 of the revised manuscript.

P13L279: → during the spring season

We have corrected accordingly. Please refer to Line 296 of the revised manuscript.

P14L281: → Asian dust storms that occurred in March-May

We have corrected accordingly. Please refer to Line 298 of the revised manuscript.

P14L283: → Local dust emissions

We have corrected accordingly. Please refer to Line 300 of the revised manuscript.

P14L289 → and nitrate, making up 4.1%

We have corrected accordingly. Please refer to Line 306 of the revised manuscript.

P14L291: contributes → contribute

We have rephrased the sentence to “Predominant Fe ion peaks possibly indicates the contribution from anthropogenic sources”. Please refer to Lines 307-308 of the revised manuscript.

P14L293-294: → ...Fe-containing residuals have presumably come from...

We have corrected accordingly. Please refer to Lines 310-311 of the revised manuscript.

P14L285: may occupied → may have occupied

We have corrected accordingly. Please refer to Line 302 of the revised manuscript.

P14L293: → Fe-containing residuals were

We have corrected accordingly. Please refer to Line 311 of the revised manuscript.

P14L299-300: → ...Na-rich particles are formed from varied sources...

We have corrected accordingly. Please refer to Lines 317-318 of the revised manuscript.

P15L305: → The continental air masses

We have corrected accordingly. Please refer to Line 323 of the revised manuscript.

P15L306: → Industrial emissions were

We have corrected accordingly. Please refer to Line 324 of the revised manuscript.

P15L308: → This might suggest that the Na-rich particles were contributed from both industrial emissions and sea salts.

We have corrected accordingly. Please refer to Lines 326-327 of the revised manuscript.

P15L318: → iron and steel products manufacturing facilities

We have corrected accordingly. Please refer to Lines 336-337 of the revised manuscript.

P15L322: → Organic carbon tends to be...

We have corrected accordingly. Please refer to Line 343 of the revised manuscript.

P15L323: wealth → worth (I am not a big fan of too many "note" phrases. There are 13 notes in this manuscript, which seems a lot. Consider making smoother transitions and better flows between sentences/paragraphs without using too many notes).

We have corrected accordingly and have detected some "note" in the revised manuscript.

P16L327: secondary inorganic species?

Secondary species contained inorganic substances (e.g., sulfate, nitrate and ammonium) and organic substances (e.g., oxalate and trimethylamine). Please refer to Figure 5 of the revised manuscript.

P16L336: → to be in the form of

We have corrected accordingly. Please refer to Line 360 of the revised manuscript.

P16L338: Low as compared to what?

Relative to nitrate (88-89%), low portions of ammonium (m/z , 18NH_4^+) in the Na-rich (23% by number) and Dust (15% by number) cloud residues were found. Please refer to Lines 362-364 of the revised manuscript.

P16L342: → in mass spectra (Figure 3)...

We have corrected accordingly. Please refer to Line 366 of the revised manuscript.

P16L343: → Thus, our data suggest that...

We have corrected accordingly. Please refer to Line 367 of the revised manuscript.

P16L340: → in two cloud residual types

We have corrected accordingly. Please refer to Line 364 of the revised manuscript.

P16L346: → In this study, we found that...

We have rephrased the sentence to “The nitrate-containing particles accounted for only 46% by number of the Aged EC cloud residues, which is significantly less than the sulfate-containing particles”. Please refer to Lines 370-371 of the revised manuscript.

P16L346: → The data indicate that nitrate-containing particles account for...

We have rephrased the sentence to “The nitrate-containing particles accounted for only 46% by number of the Aged EC cloud residues, which is significantly less than the sulfate-containing particles”. Please refer to Lines 370-371 of the revised manuscript.

P17L366: → Relatively high portions...

We have corrected accordingly. Please refer to Line 390 of the revised manuscript.

P17L368: → in the form of...

We have corrected accordingly. Please refer to Line 391 of the revised manuscript.

P17L370: → ...(Pratt et al., 2009). It may...

We have corrected accordingly. Please refer to Line 393 of the revised manuscript.

P18L373: → ...is mainly based on...

We have corrected accordingly. Please refer to Line 396 of the revised manuscript.

P18L374: → particles were internally...

We have corrected accordingly. Please refer to Line 398 of the revised manuscript.

P18L375: → ...to the K-rich type and probably...

We have corrected accordingly. Please refer to Line 399 of the revised manuscript.

P18L378: sensitive → sensitivity

We have corrected accordingly. Please refer to Line 401 of the revised manuscript.

P18L381: → Figure 6 displays the hourly... and Nf values of the nine types of...

We have corrected accordingly. Please refer to Line 404 of the revised manuscript.

P18L382-383: Awkward sentence – please rephrase.

We have modified to “The Nf of aged EC particle type showed a very abrupt increase from cloud residues to ambient particles on Jan 17.” Please refer to Lines 405-406 of the revised manuscript.

P18L386: changed → shifted

We have corrected accordingly. Please refer to Line 409 of the revised manuscript.

P19L398-400: Incomplete sentence.

We have modified to “When a cloud-free event occurred at 11:00-17:00 on 19 Jan, ambient particles remained a high level of PM_{2.5} (~ 22.7 μg m⁻³) during this period.” Please refer to Lines 421-423 of the revised manuscript.

P19L400: → The southwesterly...

We have corrected accordingly. Please refer to Line 423 of the revised manuscript.

P19L401: → from the northerly

We have corrected accordingly. Please refer to Line 424 of the revised manuscript.

P19L402: → North China or northern China (the authors use the South China word consistently in the manuscript... why not for North???)

We have corrected accordingly. Please refer to Line 425 of the revised manuscript.

P19L403: → These changes might have led...

We have corrected accordingly. Please refer to Line 426 of the revised manuscript.

P19L411-412: → we selected to analyze cloud residuals that...on 18-19 Jan as compared to cloud residuals that...

We have corrected accordingly. Please refer to Lines 431-432 of the revised manuscript.

P20L420: → for both the...

We have corrected accordingly. Please refer to Line 434 of the revised manuscript.

P20L431: → This data implies...

We have corrected accordingly. Please refer to Lines 452-453 of the revised manuscript.

P21L453: → ...with one hour intervals. The ambient...

We have corrected accordingly. Please refer to Lines 474-475 of the revised manuscript.

P21L456: → Thus, the data suggest that the initial...

We have corrected accordingly. Please refer to Line 478 of the revised manuscript.

P21L457: → cloudy air occurred around

We have corrected accordingly. Please refer to Line 479 of the revised manuscript.

P21L458: → in the size range of 200 nm up to 500 nm

We have rephrased the sentence to “A reduction of supersaturation due to entrainment of the dry northern air mass might have insufficient moisture to activate small particles, leading to unactivated particles above 0.2 μm (Figure S7)”. Please refer to Lines 479-482 of the revised manuscript.

P21L458-461: Awkward/imcomplete sentences.

We have modified to “A reduction of supersaturation due to entrainment of the dry northern air mass might have insufficient moisture to activate small particles, leading to unactivated particles above 0.2 μm (Figure S7)”. Please refer to Lines 479-482 of the revised manuscript.

P22L465: → showed that there were no significant changes

We have corrected accordingly. Please refer to Lines 485-486 of the revised manuscript.

P22L468: → as discussed in Sect. 3.3.

We have corrected accordingly. Please refer to Line 489 of the revised manuscript.

P22L473-474: do not active as CCN → are not active as CCN

We have corrected accordingly. Please refer to Lines 494-495 of the revised manuscript.

P22L478: In comparing → When comparing

We have corrected accordingly. Please refer to Line 499 of the revised manuscript.

P22L478-479: has been observed to account for → accounted for

We have corrected accordingly. Please refer to Lines 508-509 of the revised manuscript.

P22L484: → the differences

We have corrected accordingly. Please refer to Line 505 of the revised manuscript.

P23L487: → when compared to

We have corrected accordingly. Please refer to Line 508 of the revised manuscript.

P23L490: → nitrate-containing

We have corrected accordingly. Please refer to Line 511 of the revised manuscript.

P23L491: is most likely to be → possibly reflect the

We have corrected accordingly. Please refer to Line 512 of the revised manuscript.

P23L493: → confirmed that the update of gaseous HNO₃ is an...

We have corrected accordingly. Please refer to Line 514 of the revised manuscript.

P23L494: → the increased nitrate level

We have corrected accordingly. Please refer to Lines 514-515 of the revised manuscript.

P23L495: → (Figure 9), and...

We have corrected accordingly. Please refer to Line 516 of the revised manuscript.

P23L495: → in the cloud residuals

We have corrected accordingly. Please refer to Line 515 of the revised manuscript.

P23L496: → when compared with

We have corrected accordingly. Please refer to Lines 517-518 of the revised manuscript.

P24L515: We did find → There was a high fraction... amine cloud residuals found when the...

We have corrected accordingly. Please refer to Lines 534-535 of the revised manuscript.

P24L527: → The change observed in N_f

We have corrected accordingly. Please refer to Line 548 of the revised manuscript.

P24L530: induce the activation of the nuclei particles to become cloud droplets → act as CCN

We have detected the sentence due to incomplete sentence.

Figure 2: yellow rots and fire dots sound awkward...

We have modified to “The fire date (yellow dots) are available at <https://earthdata.nasa.gov/>”. Please refer to Figure 2 caption of the revised manuscript.

Figure 3: ‘of the sampled particles during the whole sampling period’ – not necessary.

We have detected accordingly. Please refer to Figure 3 caption of the revised manuscript.

Figure 7: → with an interval of one hour

We have corrected accordingly. Please refer to Figure 7 caption of the revised manuscript.

Figure 9: → ; whereas,

We have corrected accordingly. Please refer to Figure 9 caption of the revised manuscript.

References:

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1 **In situ chemical composition measurement of individual cloud residue**
2 **particles at a mountain site, South China**

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18

19 **Highlights**

- 20 1. EC-containing particles were the largest fraction of the total cloud residues (49.3% by
21 number), dominating in the range of 0.2-1.0 μm .
- 22 2. **The Nf** of the cloud residue types was influenced by air mass chemistry.
- 23 3. Amine particles represented from 0.2% to 15.1% by number of the total cloud residues
24 when air masses changed from northerly to southwesterly.
- 25 4. Compared with non-activated particles, nitrate intensity decreased in cloud residues
26 except dust type.

27 **Abstract**

28 To investigate how atmospheric aerosol particles interact with chemical composition of
29 cloud droplets, a ground-based counterflow virtual impactor (GCVI) coupled with a real-
30 time single-particle aerosol mass spectrometer (SPAMS) was used to assess the chemical
31 composition and mixing state of individual cloud residue particles in the Nanling
32 Mountain Range (1,690 m a.s.l.), South China, in Jan 2016. The cloud residues were
33 classified into nine particle types: Aged elemental carbon (EC), Potassium-rich (K-rich),
34 Amine, Dust, Pb, Fe, Organic carbon (OC), Sodium-rich (Na-rich) and Other. The largest
35 fraction of the total cloud residues was the Aged EC type (49.3% by number), followed
36 by the K-rich type (33.9% by number). Abundant Aged EC cloud residues that mixed
37 internally with inorganic salts were found in air masses from northerly polluted areas.
38 The number fraction (Nf) of the K-rich cloud residues increased within southwesterly air
39 masses from fire activities in Southeast Asia. When air masses changed from northerly
40 polluted areas to southwesterly ocean and livestock areas, the Amine particles increased
41 from 0.2% to 15.1% of the total cloud residues by number. The Dust, Fe, Pb, Na-rich and
42 OC particle types had a low contribution (0.5-4.1% by number) to the total cloud residues.
43 Higher fraction of nitrate (88-89% by number) was found in the Dust and Na-rich cloud
44 residues relative to sulfate (41-42%) and ammonium (15-23%). Higher intensity of nitrate
45 was found in the cloud residues relative to the ambient particles. Compared with non-
46 activated particles, nitrate intensity decreased in cloud residues except dust type. To our
47 knowledge, this study is the first report on **in situ** observation of the chemical
48 composition and mixing state of individual cloud residue particles in China.

49

50 Keywords: GCVI, SPAMS, cloud residues, mixing state, South China

51

52

53 **1 Introduction**

54 Aerosol-cloud interactions influence the thermodynamic and radiation balance of the
55 atmosphere (IPCC, Boucher et al., 2013). Anthropogenic particles can increase number
56 concentration of small cloud droplets, and, in turn, affect reflectivity and life time of
57 clouds (Stier et al., 2005; Lohmann et al., 2007; Rosenfeld et al., 2008). In situ cloud
58 chemical measurements have shown varied chemical composition of cloud water or
59 residues at various regions (Sorooshian et al., 2007a; Roth et al., 2016; Li et al., 2017).
60 Despite a large number of aerosol/cloud studies over the past 20 years, the uncertainty
61 for evaluating radiative forcing due to aerosol-cloud interactions has not been reduced
62 (Seinfeld. et al., 2016). Therefore, it is crucial to assess how atmospheric aerosol particles
63 contribute and interact with cloud droplets.

64 The ability of aerosol particles to act as cloud condensation nuclei (CCN) is dependent
65 on the size and chemical composition of particles at a given supersaturation (McFiggans
66 et al., 2006). Wiedensohler et al. (2009) found that the enhancement of particles CCN
67 ability was related to an increase in the average sulfate mass concentration. Dusek et al.
68 (2006) demonstrated that CCN behavior was more effected by aerosol size than chemical
69 composition. Meanwhile, aerosol mixing state also play an important role in the ability of
70 aerosol to act as CCN. It has been reported that freshly emitted elemental carbon (EC)
71 particles generally exhibit low CCN activity, whereas aged EC particles show high CCN
72 activity after experienced atmospheric processes (Zhang et al., 2008). Pratt et al. (2011)
73 found that number fractions of ammonium or oxalate internally mixed with biomass

74 burning particles increased with an aged time of 81-88 min, which promote CCN
75 behavior. Laboratory studies have shown that low-solubility organic particles internally
76 mixed with ammonium sulfate would suppress water uptake of mixed particle and thus
77 might affect CCN activity (Wise et al., 2003; Svenningsson et al., 2006; Sjogren et al.,
78 2007). An over prediction of CCN concentration by up to 35% was estimated based on
79 particle internal mixing state assumption (Medina et al., 2007; Collins et al., 2013). The
80 influence of mixing state on aerosol CCN activity varies depending on the proximity to
81 the pollution plume source and/or photochemical ageing activity (Ervens and Volkamer,
82 2010). More detailed measurements to characterize the mixing state of CCN particles
83 would improve our understanding of aerosol-cloud interactions.

84 The combined technique of a counterflow virtual impactor (CVI) and an Aerosol Mass
85 Spectrometer (AMS) or other online/offline single particle instruments is widely used to
86 characterize the chemical composition and/or mixing state of cloud/fog droplet residue
87 particles. These studies were mainly conducted in North America including Wyoming
88 (Pratt et al., 2010a), Ohio (Hayden et al., 2008), Oklahoma (Berg et al., 2009), Florida
89 (Cziczo et al., 2004; Twohy et al., 2005), California (Coggon et al., 2014), Europe
90 including Schmücke (Roth et al., 2016; Schneider et al., 2017), Jungfraujoch (Kamphus
91 et al., 2010), Åreskutan (Drewnick et al., 2007), Scandinavia (Targino et al., 2006),
92 Arctic (Zelenyuk et al., 2010), Central America (Cziczo et al., 2013), West Africa
93 (Matsuki et al., 2010) and marine areas (Twohy and Anderson 2008; Twohy et al., 2009;
94 Shingler et al., 2012).

95 Over the past three decades, China has undergone rapid economic growth accompanied
96 by increased aerosol emissions. Although scientists have worked to increase our

97 understanding of an emissions inventory and the temporal and spatial variation of
98 atmospheric aerosols in China (Zhang et al., 2012b), only few studies have employed
99 direct observation of the chemical composition and mixing state of cloud/fog droplets. Li
100 et al. (2011b) utilized transmission electron microscopy to obtain the mixing state of
101 individual ambient particles during cloud events at Mt. Tai in northern China. This result
102 showed that sulfate-related salts dominated in larger particles. Bi et al. (2016) used a
103 ground-counterflow virtual impactor (GCVI) coupled with a real-time single particle
104 aerosol mass spectrometer (SPAMS) to explore the chemical composition and mixing
105 state of individual fog residual particles at ground level in an urban area of South China.
106 They found an abundance of EC-containing particles in fog residues.

107 Here, we present a study on the chemical composition and mixing state of individual
108 cloud residue particles at a mountain site in South China. The same experimental
109 methods of Bi et al. (2016) were used in this study. The size distribution, chemical
110 composition and mixing state of cloud residues during cloud events are discussed.
111 Moreover, the chemical compositions of ambient and non-activated particles were also
112 compared with the cloud residues. The aim of this study is to assess the potential effects
113 of anthropogenic aerosols from regional transportation on cloud formation and to
114 investigate the dominant particle types in cloud droplets at a mountain site in South China.
115

116 **2 Experimental**

117 **2.1 Measurement site**

118 Our measurements were carried out during 15-26 Jan, 2016. The sampling site was
119 located in the Nanling Background Station (112° 53' 56" E, 24° 41' 56" N, 1,690 m a.s.l.)

120 at the National Air Pollution Monitoring System in South China (Figure S1). This station
121 is located at 200 km north of the metropolitan city Guangzhou and 350 km north of the
122 South China Sea (Figure S1). This site is also surrounded by a national park forest (273
123 km²), where there are scarcely any emissions from anthropogenic activities. During the
124 winter monsoon period, air pollution from northern China moves to southern China and
125 crosses the study region (Lee et al., 2005).

126

127 2.2 Instrumentation

128 In this study, a GCVI inlet system (GCVI Model 1205, Brechtel Mfg. Inc.) was used to
129 sample cloud droplets with a diameter greater than 8 μm . The ambient temperature on
130 average was 6.9 $^{\circ}\text{C}$ (ranging from -7.2 to 11.4 $^{\circ}\text{C}$) during cloud events. Only 20 cloud
131 residues that accounted for 0.08% of the total cloud residues were detected when the
132 ambient temperature was below -7 $^{\circ}\text{C}$ observed from 06:00 to 08:00 on 23 Jan. Thus,
133 cloud droplets were dominated by liquid water droplets. The measurements of the droplet
134 size spectra in this region performed during the winter of 1999-2001 showed that size of
135 cloud droplets ranged from 4 to 25 μm with average size of 10 μm and a corresponding
136 liquid water content of 0.11-0.15 g m^{-3} (Deng et al., 2007). Previous study in other
137 mountain site also showed an average size at ~ 10 μm (Borys et al., 2000). Hence,
138 assuming that size distribution of cloud droplets mostly was above 8 μm in this region.
139 The sampled cloud droplets were passed through an evaporation chamber (air flow
140 temperature at 40 $^{\circ}\text{C}$), where the associated water was removed and the dry residue
141 particles (with the air flow RH lower than 30%) remained. A stream of filtered and
142 heated ambient air (counterflow) was provided by a compressor. The particle

143 transmission efficiency of the cut size (8 μm) was 50%. The enrichment factor of the
144 particles collected by the GCVI inlet was estimated to be 5.25 based on theoretical
145 calculation (Shingler et al., 2012). Ambient particles were collected through an ambient
146 inlet with a cut-off aerodynamic diameter (d_a) of 2.5 μm when cloud-free periods were
147 present. Non-activated (interstitial) particles were sampled through the ambient inlet
148 during the cloud events in this study. The ambient or non-activated particles inlet was
149 dried using a silica gel diffusion dryer. During cloud-free periods, a ratio of particle
150 concentration measured behind the CVI (below 1 cm^{-3}) to ambient aerosol concentration
151 (2,000 cm^{-3}) was 0.0005, indicating that instances of particle breakthrough and small
152 particle contamination were absent. The cloud droplet residues, ambient or non-activated
153 particles were subsequently analyzed by a suite of aerosol measurement devices,
154 including a SPAMS (Hexin Analytical Instrument Co., Ltd., Guangzhou, China), a
155 scanning mobility particle sizer (SMPS) (MSP Cooperation) and an aethalometer (AE-33,
156 Magee Scientific Inc.).

157 A detailed operational principle of the SPAMS has been described elsewhere (Li et al.,
158 2011a). Briefly, aerosol particles are drawn into SPAMS through a critical orifice. The
159 particles are focused and aerodynamically sized by two continuous diode Nd:YAG laser
160 beams (532 nm). The particles are subsequently desorbed/ionized by a pulsed laser (266
161 nm) triggered exactly based on the velocity of the specific particle. The positive and
162 negative ions generated are recorded with the corresponding size of individual particles.
163 Polystyrene latex spheres (Nanosphere Size Standards, Duke Scientific Corp., Palo Alto)
164 of 0.2-2.0 μm in diameter were used to calibrate the sizes of the detected particles. The
165 ambient pressure was 830 hPa (826-842 hPa) during the measurements and the

166 calibration. Particles measured by SPAMS mostly fell within the size range of d_{va} 0.2-2.0
167 μm (Li et al., 2011a).

168

169 **2.3 Definition of cloud events**

170 To reliably identify the presence of cloud events, an upper-limit visibility threshold of 5
171 km and a lower-limit relative humidity (RH) threshold of 95% were set in the GCVI
172 software (Bi et al., 2016). Three long-lasting cloud events occurred during the periods of
173 16:00 (local time) 15 Jan - 07:00 17 Jan (cloud I), 20:00 18 Jan - 12:00 19 Jan (cloud II)
174 and 17:00 19 Jan - 13:00 23 Jan (cloud III), as marked in Figure 1. In addition, a cloud
175 event occurred at 14:40 - 15:00 on 17 Jan, but we did not do an analysis due to the short
176 duration. The measured cloud residual concentration was integrated by the SMPS and

177 was then corrected by the enrichment factor and transmission efficiency of the GCVI.

178 The corrected cloud residual concentrations on average were 436 cm^{-3} , 568 cm^{-3} and 544
179 cm^{-3} for cloud I, cloud II and cloud III, respectively (Figure S2). From 10:00 21 Jan to

180 13:00 23 Jan, cloud residues and non-activated particles were alternately sampled with an
181 interval of one hour. During this period, a ratio of number residues to total number
182 particles (sum of cloud residues and non-activated particle) on average was 0.43 ± 0.20 .

183 Low levels of $\text{PM}_{2.5}$ ($\sim 12.7\ \mu\text{g m}^{-3}$) exclude the influence of hazy days. A rainfall
184 detector of the GCVI system was also used to exclude rain droplet contamination. When
185 cloud events occurred without precipitation, sampling was automatically triggered by the
186 GCVI control software (Bi et al., 2016).

187

188

189 **2.4 Particle classification**

190 During this study period, a total of 73,996 particles including 49,322 ambient, 23,611
191 cloud residual and 1,063 non-activated particles with bipolar mass spectra were
192 chemically analyzed in the size range of d_{va} 0.2-1.9 μm . The sampled particles were
193 firstly classified into 101 clusters using an Adaptive Resonance Theory neural network
194 (ART-2a) with a vigilance factor of 0.75, a learning rate of 0.05, and 20 iterations (Song
195 et al., 1999). Then by manually combining similar clusters, eight major particle types
196 Aged EC, Potassium-rich (K-rich), Amine, Dust, Fe, Pb, Organic carbon (OC), and
197 Sodium-rich (Na-rich) with distinct chemical patterns were obtained, which represented
198 ~99.9% of the population of the detected particles. The remaining particles were grouped
199 together as “Other”. Assuming that the number of individual particles followed Poisson
200 distribution, standard errors for number fraction of particle type were estimated (Pratt et
201 al., 2010a).

202

203 **3 Results and discussion**

204 **3.1 Back trajectories and meteorological conditions**

205 Back trajectories in this study were calculated using the Hybrid Single Particle
206 Lagrangian Integrated Trajectory (HYSPLIT Model). A height of the HYSPLIT model in
207 the study region (a spatial resolution of $0.5^\circ \times 0.5^\circ$) is averaged 500 m a.s.l., lower than
208 height of the observed site (1,690 m a.s.l.). Thus, a height of 1,800 m a.s.l.
209 (approximately 100 m above the observed site) was chosen as an endpoint in the model.
210 The station was mainly affected by southwesterly or northerly air masses in this study
211 (Figure 2). In addition, the beginning altitude of the southwesterly air masses traversed at

212 lower heights relative to the northerly air masses (Figure 2). The southwesterly air masses,
213 accompanied by warm moist airflows, occurred during 15-17 and 20-21 Jan, which
214 promoted high RH condition (Figure 1). Conversely, the northerly air masses, associated
215 with cool dry airstreams, occurred during 18 and 23-24 Jan and led to a decrease in
216 temperature and relative humidity. Note that, on 18-19 and 22-23 Jan, the air mass
217 encountered initial mixing of northerly cloud-free air and southwesterly cloudy air.
218 Entrainment of nuclei particles originated from northern air masses might be activated to
219 cloud droplets (Sect. 3.4).

220 Meteorological conditions were unstable, with high southwesterly flow ($\sim 6.5 \text{ m s}^{-1}$)
221 during 15-17 and 20-22 Jan (Figure 1). The level of $\text{PM}_{2.5}$ remained a low value of
222 approximately $3 \mu\text{g m}^{-3}$ for this time period. A high level of $\text{PM}_{2.5}$ ($\sim 20 \mu\text{g m}^{-3}$) was
223 observed during 18 Jan when the northerly flow dominated. Similarly, the average $\text{PM}_{2.5}$
224 value reached $24 \mu\text{g m}^{-3}$ during 24 Jan. Although the local northerly and southwesterly
225 flows occurred alternately, the particles were still originated from the northerly air mass
226 for this period (Figure 2). During 23-24 Jan, a sharp decrease in temperature (Figure 1)
227 was observed due to a cold wave associated with a violent northerly flow. The wind
228 speed during the cold wave exceeded the upper-limit speed ($\sim 12 \text{ m/s}$) of a wind speed
229 sensor.

230

231 3.2 The chemical characterization of cloud droplet residues

232 Figure 3 shows the average positive and negative mass spectra of the main six particle
233 types. The Aged EC particles were characterized by EC cluster ions (e.g., $m/z \pm 12\text{C}^{+/-}$,
234 $\pm 36\text{C}_3^{+/-}$, $\pm 48\text{C}_4^{+/-}$, $\pm 60\text{C}_5^{+/-}$, ...) and a strong K^+ ion signal ($m/z 39\text{K}^+$) as well as a

235 sulfate ion signal (m/z -97HSO₄⁻), and some minor organic markers (m/z 27C₂H₃⁺,
236 43C₂H₃O⁺) (Moffet and Prather, 2009). EC particles mainly originated from combustion
237 processes (Bond et al., 2013). The strong K⁺ ion signal in the Aged EC particles implies
238 partially originated from biomass burning sources (Bi et al. 2011). The Aged EC particle
239 type was the largest fraction (49.3% by number) of the total cloud residues (Figure S3).
240 In addition, number fraction (Nf) of the Aged EC residues significantly decreased from
241 54.1% in the size range of 0.2-1.0 μm to 19.2% in the size range of 1.1-1.9 μm (Figure 4).
242 Note that the chemical composition of cloud residues is dependent on the particle size
243 (Roth et al., 2016), and the number reported for each particle type might suffer from the
244 bias related to size-dependent transmission efficiency (Qin et al., 2006). The relative
245 fraction of cloud residues in 0.1 μm size interval is presented to minimize the influence of
246 size-dependent transmission efficiency of single particle mass spectrometry (Roth et al.,
247 2016).

248 The K-rich particles exhibited the highest peak at m/z 39K⁺, mainly combined with
249 sulfate and nitrate (m/z -46NO₂⁻, -62NO₃⁻) and presumably derived from biomass/biofuel
250 burning source (Moffet et al., 2008; Pratt et al. 2011; Zhang et al., 2013). An aged time
251 of 81-88 min biomass burning particles were found to show an increase in the mass
252 fractions of ammonium, sulfate, and nitrate (Pratt et al. 2011). In this study, the K-rich
253 particles would be expected to experience aged process due to strong sulfate and nitrate
254 signals (Hudson et al. 2004; Pratt et al. 2011). Aged biomass burning particles can
255 participate in cloud droplets formation and show an effective CCN activity (Pratt et al.
256 2010a). The K-rich particle type, the second largest contributor, accounted for 33.9% by
257 number of the total cloud residues (Figure S3).

258 The abundant aged soot/EC and biomass burning particles were often detected in
259 cloud residues (Pratt et al., 2010a; Roth et al., 2016). The contribution of local
260 anthropogenic origins to aged soot and/or biomass burning particles in cloud/fog residues
261 has been reported in Schmücke (Roth et al., 2016) and Guangzhou city (Bi et al., 2016).
262 At the North Slope of Alaska, the measurement of biomass burning particles in cloud
263 residues mainly resulted from local vicinity or as far away as Siberia and Asian sources
264 (Zelenyuk et al., 2010; Hiranuma et al., 2013). Similarly, the majority of Aged EC and K-
265 rich cloud residues observed here are expected to originate from long-range
266 transportation due to insignificant sources of local anthropogenic emissions and the fire
267 dots (Figure 2). At the Jungfraujoch station (3,580 m a.s.l.) in Europe, the K-rich
268 (biomass burning) particles only contributed 3% of the cloud droplets, and the Aged EC
269 residuals were insignificant (<1% by number) (Kamphus et al., 2010). The Jungfraujoch
270 station is predominantly within the free tropospheric condition, such that the biomass
271 burning contribution can be expected to be lower than at other sites.

272 The Amine particles were characterized by related amine ion signals at m/z
273 $58\text{C}_2\text{H}_5\text{NHCH}_2^+$ (diethylamine, DEA), $59\text{N}(\text{CH}_3)_3^+$ (trimethylamine, TMA) and
274 $86\text{C}_5\text{H}_{12}\text{N}^+$ (triethylamine, TEA) (Angelino et al., 2001; Moffet et al., 2008). This
275 particle type also contained sulfuric acid ion signals at m/z $-195\text{H}(\text{HSO}_4)_2^-$, indicative of
276 acidic particles (Rehbein et al., 2011). The Amine particles represented 3.8% by number
277 of the total cloud residues (Figure S3). Higher N_f of the Amine residues was detected in
278 the size range from 0.7 to 1.9 μm relative to the size range from 0.2 to 0.6 μm (16.7%
279 versus 0.4%), as shown in Figure 4. Aqueous reactions improving the participation of
280 amine have been observed in Guangzhou (Zhang et al., 2012a) and Southern Ontario

281 (Rehbein et al., 2011). A recent study also showed a clear enhancement of amine-
282 containing particles in cloud residues compared to the ambient particles (9% versus 2%
283 by number) (Roth et al., 2016). It indicates a preferential formation of amine within the
284 cloud, which is in contrast to the observations of Bi et al. (2016). It might suggest that
285 enhancement of particle amine is not only depend on high RH or fog/cloud process, but
286 also sensitive to other parameters, such as presence of gas phase amine source (Rehbein
287 et al., 2011).

288 The Dust particles presented significant ions at m/z 40Ca^+ , $56\text{CaO}^+/\text{Fe}^+$, $96\text{Ca}_2\text{O}^+$
289 and -76SiO_3^- and sulfate as well as nitrate markers. Previous studies showed that dust
290 particles that are internally mixed with sulfate and nitrate are expected to act as CCN
291 (Twohy and Anderson 2008; Twohy et al., 2009), despite sulfate and nitrate partial
292 formation from in-cloud production. This type contributed 2.9% by number of the total
293 cloud residues (Figure S3). A slight increase in N_f of the Dust residues was observed in
294 size range above $0.5\ \mu\text{m}$ relative to that below $0.5\ \mu\text{m}$ (3.0% versus 1.0% by number). At
295 Mt. Tai in northern China, a high concentration of Ca^{2+} in cloud/fog water was mainly
296 attributed to a sandstorm event during the spring season (Wang et al., 2011). At Mt. Heng
297 in southern China, the abundant crust-related elements (e.g., Al) observed in cloud water
298 is due to Asian dust storms that occurred in March-May (Li et al., 2017). Based on the
299 backward trajectory, the site was unlikely affected by sandstorm source in northwestern
300 China during the cloud events. Local dust emissions by anthropogenic-disturbing soils or
301 removing vegetation cover can be excluded as a result of forest protection. Additionally,
302 dust residues may have occupied larger CCN (Tang et al., 2016), which cannot be

303 detected by the SPAMS. Hence, a low fraction (2.9% by number) of dust cloud residue
304 might be due to the limitation of the SPAMS.

305 The Fe particles had its typical ions at m/z 56Fe^+ and internally mixed with sulfate
306 and nitrate, made up 4.1% by number of the total cloud residues. Approximately 16% of
307 the Fe cloud residues contained Ca^+ peak (m/z 40). Predominant Fe ion peaks possibly
308 indicates the contribution from anthropogenic sources (Zhang et al., 2014), especially the
309 northern air masses across iron/steel industrial activities in Yangtze River Mid-Reaches
310 city clusters (Figure 2). The contribution of anthropogenic and natural Fe-containing
311 particles sources (Moteki et al., 2017) to observed Fe-containing residues is expected.
312 The presence of Fe in the cloud droplets play an important role in aqueous-phase SO_2
313 catalytic oxidation in cloud processing (Harris et al., 2013), thus accelerating the sulfate
314 content of Fe-containing particles in cloud processing.

315 The Na-rich particles were mainly composed of ion peaks at m/z 23Na^+ and 39K^+ in
316 the positive mass spectra, and nitrate and sulfate species in the negative mass spectra,
317 made up 3.0% by number of the total cloud residues. Na-rich particles are formed from
318 varied sources including industrial emissions, sea salt or dry lake beds (Moffet et al.
319 2008). The Nf of Na-rich cloud residues did not increase from continental (Northerly) air
320 mass on 19 Jan to maritime (southwesterly) air mass on 21 Jan (3.3% versus 2.4% by
321 number). However, the related sea salt ion peak area (m/z , $81/83 \text{Na}_2^{35}\text{Cl}^+/\text{Na}_2^{37}\text{Cl}^+$) were
322 enhanced for Na-rich particles origination from maritime air mass relative to continental
323 air mass (3.8 ± 2.4 times). The continental air masses crossed industrial areas where the
324 Yangtze River Mid-Reaches city cluster is located (Figure 2). Industrial emissions were a
325 possible contributor to Na-rich particles under the influence of continental air masses

326 (Wang et al. 2016). This might suggest that the Na-rich particles were originated from
327 both industrial emissions and sea salts.

328 The OC, Pb and Other particle types contributed 0.1%-2.3% by number to the total
329 cloud residues (Figure S3). Their average mass spectra can be found in Figure S4. The
330 OC particles presented dominant intense OC signals (e.g., m/z $27C_2H_3^+$, $37C_3H^+$,
331 $43C_2H_3O^+$ and $51C_4H_3^+$) and abundant sulfate. Presence of K^+ signal was found in the
332 OC particles, suggesting possible biomass burning sources (Bi et al. 2011). OC particles
333 might exist in smaller cloud residues (Sellegri et al., 2003a), which cannot be detected by
334 the SPAMS. The Pb particles showed its typical ions at m/z $208Pb^+$ and internally mixed
335 with K^+ and Cl^- . Previous studies have found that K and Cl internally mixed with Pb
336 particles have a possible origination of waste incineration (Zhang et al., 2009) or iron and
337 steel products manufacturing facilities (Tsai et al., 2007). Only three particles were found
338 containing calcium, organic carbon, organic nitrogen and phosphate ion signals, implying
339 a possible existence of biological particles (Pratt et al., 2009a). Such particles were
340 classified as the Other type due to low number.

341 Previous measurements have found that dust, playa salts, sea salt or metal particles
342 were often enriched in larger cloud droplets ($\sim 20 \mu m$) (Bator and Collett, 1997; Moore et
343 al., 2004; Pratt et al., 2010b). Organic carbon tended to be enriched in small cloud/fog
344 droplets, extending to $4 \mu m$ (Herckes et al., 2013). The size of cloud droplets were above
345 $8 \mu m$ in the present study. Additionally, the particle transmission efficiency increased
346 with increasing cloud droplet size (Shingler et al., 2012). Thus, it partially leads to
347 relatively larger fractions of the observed Dust, Na-rich and metal cloud residues, and the
348 less fraction of the OC cloud residues in this study.

349 3.3 Mixing state of secondary species in cloud residues

350 The high Nfs of sulfate-containing particles were found in the K-rich (91%), OC (100%),
351 Aged EC (98%), Pb (74%), Fe (93%) and Amine (99%) cloud residues, as shown in
352 Figure 5. Lower Nfs of sulfate-containing particles were observed in the Na-rich (41%)
353 and Dust (42%) cloud residues. In contrast, nitrate-containing particles contributed 89%
354 and 88% by number to the Na-rich and Dust cloud residues, respectively. The acid
355 displacement reaction of sea salt chloride (Na-rich particles) by HNO₃ might lead to a
356 depletion of chloride and enhancement of nitrate (Laskin et al., 2012). Similarly, the
357 heterogeneous chemistry of HNO₃ in the dust particles also contributes the preferential
358 enrichment of nitrate (Tang et al., 2016). Moreover, after activation, uptake of gas-phase
359 HNO₃ would increase nitrate level in the cloud residues (Schneider et al., 2017). The
360 nitrate in the cloud residues was thought to be in the form of ammonium nitrate by
361 estimating the ratio of m/z 30 to m/z 46 in AMS data (Drewnick et al., 2007; Hayden et
362 al., 2008). Relative to nitrate, low portions of ammonium (m/z, 18NH₄⁺) in the Na-rich
363 (23% by number) and Dust (15% by number) cloud residues suggest that in this region,
364 ammonium nitrate was not a predominant form of nitrate in the two cloud residual types.
365 The Na-rich and Dust types were mainly composed of alkaline ion peaks (m/z, 23Na⁺,
366 39K⁺ and 40Ca⁺) in position mass spectra (Figure 3), accompanied with larger fraction
367 (88-89%) of nitrate. Thus, our data suggests that nitrate might exist in the form of
368 Ca(NO₃)₂, NaNO₃ or KNO₃ in the Dust and Na-rich cloud residues. It should be noted
369 that the evaporation chamber of the GCVI may lead to a reduction of ammonium nitrate
370 in the cloud residues (Hayden et al., 2008). The nitrate-containing particles accounted for
371 only 46% by number of the Aged EC cloud residues, which is significantly less than the

372 sulfate-containing particles. Previous field studies have found that Aged EC (soot)
373 fog/cloud residues are mainly internally mixed with sulfate (Pratt et al., 2010a; Harris et
374 al., 2014; Bi et al., 2016). Aged EC particles mixed with sulfate are good CCN, rather
375 than formed by in-cloud processing (Bi et al., 2016; Roth et al., 2016). Laboratory
376 measurements have also demonstrated that EC particles internally mixed with sulfate
377 showed a high hygroscopic behavior and thus affect CCN ability (McMeeking et al.,
378 2011). High portions (75-86% by number) of ammonium-containing particles were
379 observed for the OC and Aged EC cloud residues, suggesting that ammonium will mostly
380 be in the form of ammonium sulfate or ammonium nitrate for two cloud residual types
381 (Zhang et al., 2017). This result also implies that ammonium-containing particles are
382 preferentially activated or enhanced uptake of gaseous NH_3 to neutralize acidic cloud
383 droplets for the OC and EC types.

384 Water soluble organics (e.g., amine and oxalate) have previously been measured in
385 cloud water/residues (Sellegrri et al., 2003b; Sorooshian et al., 2007a; Pratt et al., 2010a).
386 The presence of TMA (93% by number) in the Amine cloud residues is expected to
387 promote water uptake activity (Sorooshian et al., 2007b). A total of 3,410 oxalate-
388 containing particles (m/z , $-89\text{HC}_2\text{O}_4^-$) represented 14.4% by number of the total cloud
389 residues, which was mainly associated with the K-rich cloud residues (~70% by number).
390 Oxalate-containing particles (~30% by number) in the metal (Pb, Fe) cloud residues
391 might be in the form of metal oxalate complexes from reactions of in-cloud formation
392 oxalate with metals (Furukawa and Takahashi, 2011). Oxalate can readily partition into
393 the particle phase to form amine salts (Pratt et al., 2009b). It may facilitate the
394 entrainment of oxalate (33% by number) in the Amine residues. A low fraction (4%) of

395 oxalate-containing particles in the OC type is a result of restrictive classification.
396 Classification of the OC particles is mainly based on intense organic carbon ion signals
397 (e.g., m/z $27C_2H_3^+$, $37C_3H^+$, $43C_2H_3O^+$ and $51C_4H_3^+$). The majority of oxalate-containing
398 particles were internally mixed with the K-rich type. Therefore, oxalate was classified to
399 the K-rich type and probably contributed from biomass burning. The K-rich particles
400 could contain an abundant of organics (Pratt et al. 2011), however, the signals of organics
401 were covered by the potassium due to its high sensitivity to the laser.

402

403 3.4 Comparison of cloud residues in different air mass sources

404 Figure 6 displays the hourly detected particle counts and Nf values of the nine types of
405 cloud residues and ambient particles. The Nf of the Aged EC type showed a very abrupt
406 increase from cloud residues to ambient particles on Jan 17. The ambient RH showed an
407 abrupt decrease from nearly 100% at 10:00 to 85% at 11:00 on 17 Jan (Figure 1). The
408 ambient temperature also decreased from 10 °C at 11:00 to 4 °C at 18:00 on 17 Jan
409 (Figure 1). These changes imply that the air mass shifted from southwesterly cloudy air
410 to northerly cloud-free air around noon on 17 Jan (Figure 2). The entrained particles
411 originated from northern air mass might have insufficient supersaturation to be activated
412 as cloud droplets. It resulted in the remarkable increase of the Aged EC particles in
413 ambient particles on Jan 17 (Figure 6).

414 The ambient RH increased from 60% at 19:00 to nearly 100% at 21:00 on 18 Jan
415 (Figure 1). The ambient temperature also increased from 1.3 °C at 22:00 on 18 Jan to
416 3.2 °C at 06:00 on 19 Jan (Figure 1). These changes imply that the air mass changed from
417 northerly cloud-free air to southwesterly cloudy air at night on 18 Jan (Figure 2). During

418 18-19 Jan, the cloud residues and ambient particles showed similar chemical
419 characteristics and were dominated by Aged EC particles (Figure 6). A lack of significant
420 variation in the particle types for this period suggests that nuclei particles originated from
421 northerly cloud-free air could be activated to become cloud droplets. When a cloud-free
422 event occurred at 11:00-17:00 on 19 Jan, ambient particles remained a high level of $PM_{2.5}$
423 ($\sim 22.7 \mu\text{g m}^{-3}$). The southwesterly wind flow on 19-20 Jan was too weak ($\sim 2.75 \text{ m s}^{-1}$)
424 to dilute particles originated from the northerly air masses (Figure 1). Additionally, a
425 high RH (90%) air mass at height 1,500 m (a.s.l.) gradually moved to northern China
426 from 19 to 20 Jan (Figure S5). These changes might have led to similar residual particle
427 types observed from 19 Jan to 20 Jan, although the site encountered southwesterly cloudy
428 air on 19-20 Jan (Figure 2).

429 As mentioned above, the Nf of the cloud residue types significantly changed as the
430 air mass origin varied from northerly to southwesterly. To further investigate the
431 influence of air mass history, we selected to analyze cloud residues that had arrived from
432 a northerly air mass on 18-19 Jan as compared to cloud residues that originating from a
433 southwesterly air mass during the periods of 16-17 and 21-22 Jan. The detected number
434 of cloud residues for both the northerly and southwesterly air masses are given in Table
435 S1. The southwesterly air masses accompanied by high relative humidity (90%) (Figure
436 S5) may have triggered particles activated to CCN prior to their arrival to the sampling
437 site.

438 The K-rich type was found to contribute 23.9% to the cloud residues in the northerly
439 air mass, which was significantly lower than its contribution to the southwesterly air mass
440 (51.5%), as shown in Figure 7. A similarity in averaged mass spectrum of the K-rich

441 residues was found for the southwesterly and northerly air masses (Figure S6). The
442 considerable increase of K-rich cloud residues suggests a major influence of regional
443 biomass-burning activities. Biomass-burning emissions from Southeast Asia, including
444 Myanmar, Vietnam, Laos and Thailand, where abundant fire dots are observed (Figure 2),
445 could have been transported to the sampling site under a southwesterly air mass (Duncan
446 et al., 2003). In contrast, the Aged EC type represented only 23.7% of the cloud residues
447 under the influence of the southwesterly air mass, which was significantly lower than
448 observations for the northerly air mass (59.9%), as shown in Figure 7. This result
449 suggests that the northern air mass has a greater influence on the presence of Aged EC
450 cloud residues.

451 An obvious increase in Nf of the Amine type was observed in the southwesterly air
452 mass (15.1%) compared to the northerly air mass (0.2%), as shown in Figure 7. This data
453 implies that the sources or formation mechanisms of amine in cloud residues varied in
454 different air masses. The southwesterly air masses arrived from as far as the Bay of
455 Bengal and then travelled through Southeast Asia region before reaching South China
456 (Figure 2). The potential gas amine emissions from ocean (Facchini et al., 2008) and
457 livestock areas (90 million animals, data was available at the website
458 <http://faostat3.fao.org>) in Southeast Asia region might promote the enrichment of amine
459 particles. Furthermore, after activation, the partitioning of the gas amine on cloud
460 droplets may further contribute to the enhanced Amine cloud residues (Rehbein et al.,
461 2011), especially for air masses delivered via routes with high relative humidity, as
462 mentioned above (Figure S5). In contrast, northerly air mass accompanied with dry

463 airstreams may unfavorably induce the partitioning of gas amines into the particle phase
464 (Rehbein et al., 2011).

465

466 **3.5 Comparison of cloud residues with ambient and non-activated particles**

467 A direct comparison between cloud residues and ambient particles was limited because of
468 their differences in air mass origins. During the sampling period, the cloud events
469 occurred once the southwesterly air masses were dominant. Hence a comparison between
470 cloud residues and ambient particles cannot be addressed under the influence of
471 southwesterly air masses. Here, we chose five hours before and after the beginning of the
472 cloud II period in order to compare cloud residues and ambient particles with similar
473 northerly air mass origins, as discussed in Sect. 3.4.

474 The cloud residues and non-activated particles were alternately sampled with an
475 interval of one hour from 21 Jan to 23 Jan. The ambient temperature decreased from 6 °C
476 at 11:00 to 0 °C at 23:00 on 22 Jan (Figure 1). Ambient particles level (sum of residual
477 and non-activated particles) showed a clearly increase from 156 cm⁻³ to 1460 cm⁻³ during
478 this period (Figure S2). Thus, the data suggests that the initial mixing of northerly cloud-
479 free air and southwesterly cloudy air occurred around noon on 22 Jan. A reduction of
480 supersaturation due to entrainment of the dry northern air mass might have insufficient
481 moisture to activate small particles, leading to unactivated particles above 0.2 μm
482 (Figure S7) (Mertes et al., 2005; Kleinman et al., 2012; Hammer et al., 2014), which can
483 be detected by the SPAMS.

484 The contribution of K-rich particles in cloud residues (23.9%) slightly decreased
485 relative to ambient particles (30.7%), as shown in Figure 7. Previous studies have found

486 that there were no significant changes in Nf of biomass-burning particles for cloud
487 residues relative to ambient particles (Pratt et al., 2010a; Roth et al., 2016). The biomass-
488 burning particles internally mixed with soluble species (e.g., sulfate, nitrate and oxalate)
489 enhanced their ability to act as CCN, as discussed in Sect. 3.3. Kamphus et al. (2010)
490 reported that biomass-burning particles account for only 3% of cloud residues compared
491 with 43% of ambient particles, and they suspected that biomass-burning particles might
492 exist in the form of tar balls (hydrophobic materials). A slight increase in Nf of the Aged
493 EC cloud residues (59.9%) was observed relative to ambient particles (53.8%), as shown
494 in Figure 7. In general, freshly emitted EC particles are less hydrophilic and are not
495 active as CCN (Bond et al., 2013). The Aged EC particles show a high degree of internal
496 mixing with secondary inorganic compounds in this study (Figure 5), improving their
497 ability to act as CCN. The remaining particle types showed no clear differences in Nf
498 between cloud residues and ambient particles.

499 When comparing the cloud residues with non-activated particles, a significant change
500 in Nf was found for the Aged EC and K-rich type. A higher Nf of K-rich particles and a
501 lower Nf of EC particles were found for the cloud residues relative to the non-activated
502 particles (Figure 7). Entrainment of northerly cloud-free air might lower supersaturation
503 during this period. Aged EC particles may require very high supersaturation to grow into
504 cloud droplets and thus, only form hydrated non-activated aerosol (Hallberg et al., 1994).

505 Figure 8 and 9 show the differences in average mass spectra for cloud residues
506 versus ambient particles, as well as cloud residues versus non-activated particles,
507 respectively. Nitrate intensity (average ion peak area) enhanced in the cloud residues
508 when compared to ambient particles. In addition, nitrate-containing particles accounted

509 for 70% of the cloud residues compared to 38% of the ambient particles. Drewnick et al.
510 (2007) suggested that rather than sulfate, high nitrate content in pre-existing particles
511 preferentially acted as cloud droplets. Compared with nitrate-containing ambient particles,
512 larger size of containing-nitrate residues (Figure S8) possibly reflect the uptake of
513 gaseous HNO₃ during cloud process (Hayden et al. 2008; Roth et al., 2016). A recent
514 study also confirmed that the uptake of gaseous HNO₃ is an important contributor for the
515 increased nitrate level in the cloud residuals (Schneider et al., 2017). Interestingly, we
516 observed a decrease in nitrate intensity in cloud residues except dust type (Figure 9), and
517 a large size distribution of nitrate-containing cloud residues (Figure S7) when compared
518 with non-activated particles. This result suggests that particle size, rather than nitrate
519 content, plays a more important role in the activation of particles into cloud droplets.

520 Sulfate intensity enhancement was only observed in the OC cloud residues relative to
521 both ambient and non-activated particles. Although the in-cloud addition of sulfate can be
522 produced from aqueous Fe-catalyzed or oxidation by H₂O₂/O₃ reactions (Harris et al.,
523 2014), sulfate abundance was found in the Fe cloud residues relative to non-activated
524 particles, but no enhancement relative to ambient particles. Previous studies also showed
525 that the mass or number fraction of sulfate-containing particles in the cloud residues
526 changed between ambient and non-activated particles (Drewnick et al., 2007; Twohy and
527 Anderson, 2008; Schneider et al., 2017). However, the reason for these changes remains
528 unclear.

529 The in-cloud process has been reported to be an important pathway for the production
530 of amine particles (Rehbein et al., 2011; Zhang et al., 2012a). In this study, no
531 remarkable change in Nf of the Amine cloud residues was obtained relative to the

532 ambient particles (0.2% versus 0.2% by number), as shown in Figure 7. The absence of
533 amine species in cloud residues may be partially affected by droplet evaporation in the
534 GCVI (Bi et al., 2016). However, there was a high fraction of the amine cloud residuals
535 when the southwesterly air mass prevailed, as discussed in Sect. 3.4. A lack of gas-phase
536 amines may be the cause of few amine particles detected in the ambient particles and
537 cloud residues (Rehbein et al., 2011). An increase in Nf of cloud residues was observed
538 compared with non-activated particles (5.2% versus 0.1% by number), as shown in
539 Figure 7. An increase of particle water content facilitates partitioning of gas-phase amine
540 species into the aqueous phase when gas-phase amines present (Rehbein et al., 2011).

541

542 **4 Conclusions**

543 This study presented an in situ observation of individual cloud residues, non-
544 activated and ambient particles at a mountain site in South China. The finding shows that
545 the Aged EC (49.3%) and K-rich types (33.9%) dominate the cloud residues in a remote
546 area of China, followed by the Fe (4.1%), Amine (3.8%), Na-rich (3.0%) and Dust (2.9%)
547 types. The OC, Pb and Other types contributed 0.1%-2.3% by number to the total cloud
548 residues. The observed change in Nf of the cloud residue types, influenced by various air
549 masses, highlights the important role of regional transportation in the observed cloud
550 residual chemistry. Amine particles represented from 0.2% to 15.1% by number of the
551 total cloud residues dependent on the air mass history. Sulfate was found to be highly
552 mixed with the K-rich, OC, Aged EC, Pb, Fe and Amine cloud residues, while nitrate was
553 highly mixed with the Na-rich and Dust cloud residues. Compared with non-activated
554 particles, nitrate intensity decreased in cloud residues except dust type, and sulfate

555 intensity enhancement was only observed in the OC and Fe cloud residues.

556

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566

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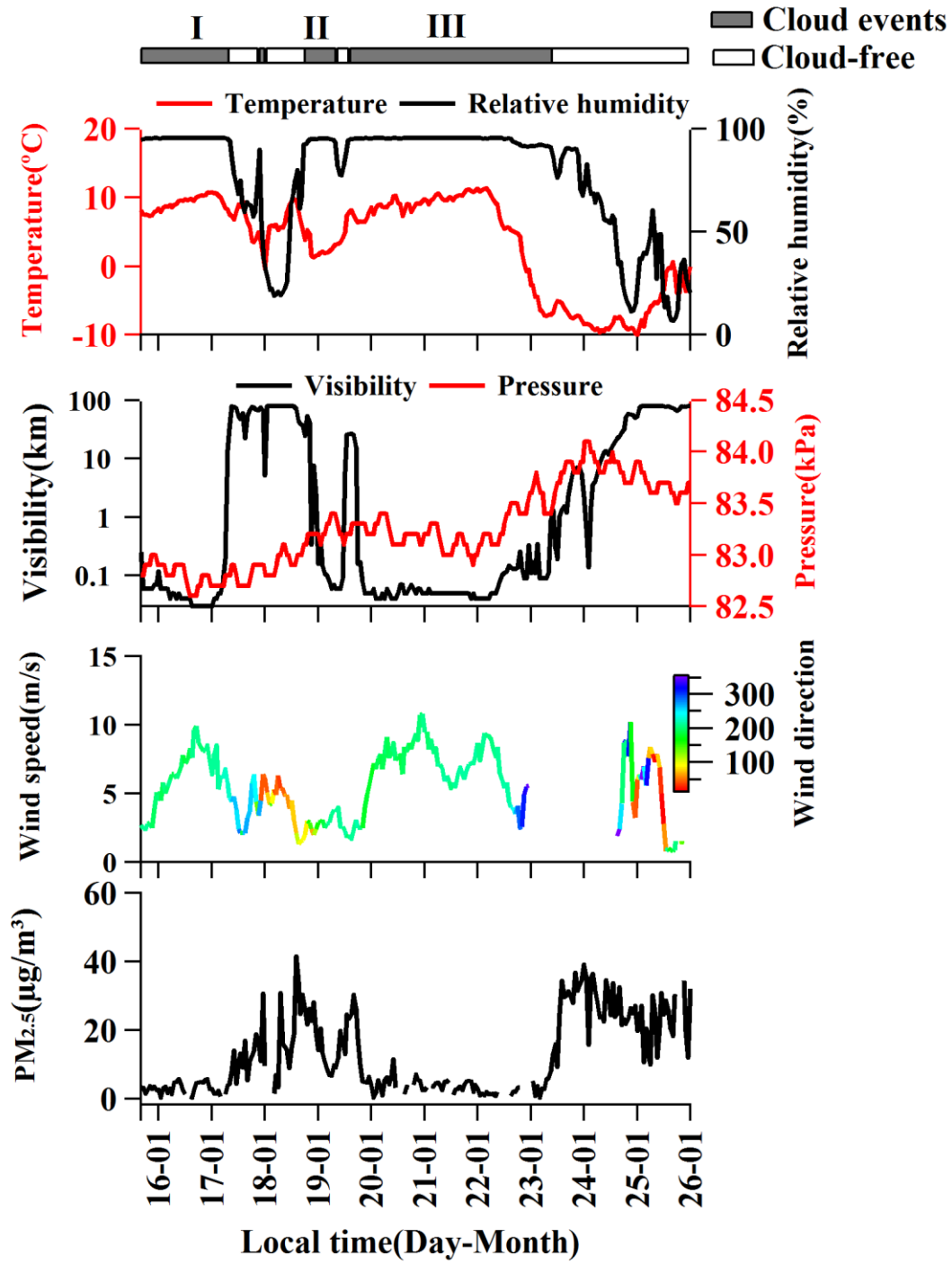
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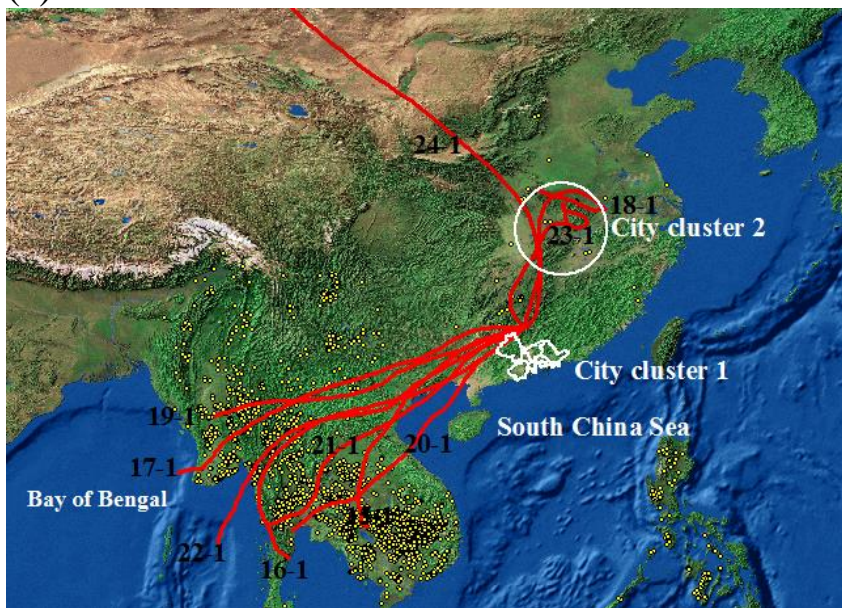
876 Figure 1: The hourly average variations in meteorological conditions (temperature,

877 relative humidity, visibility, pressure, wind speed and direction) and PM_{2.5}.

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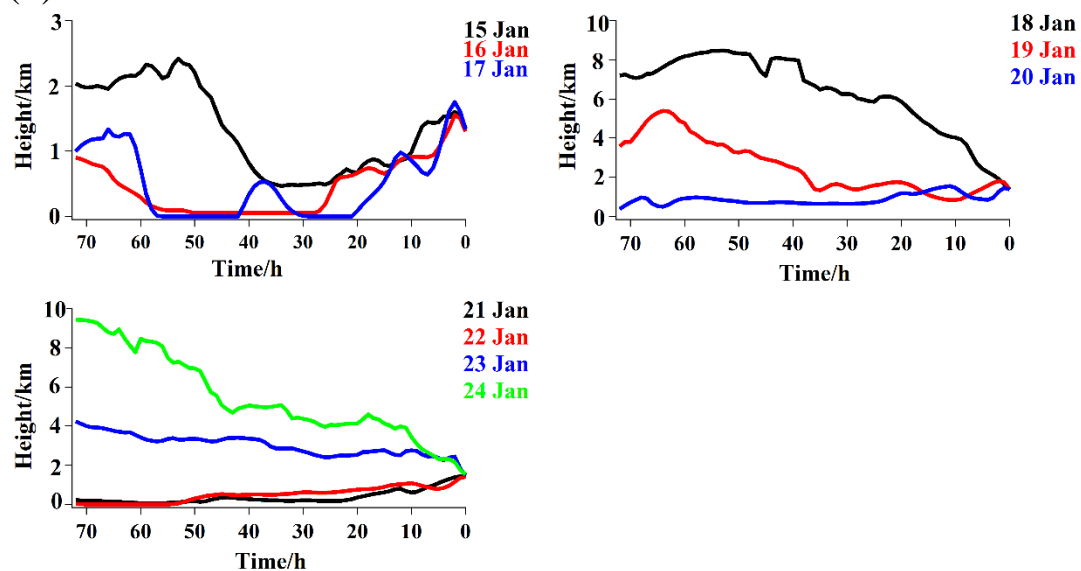
(a)



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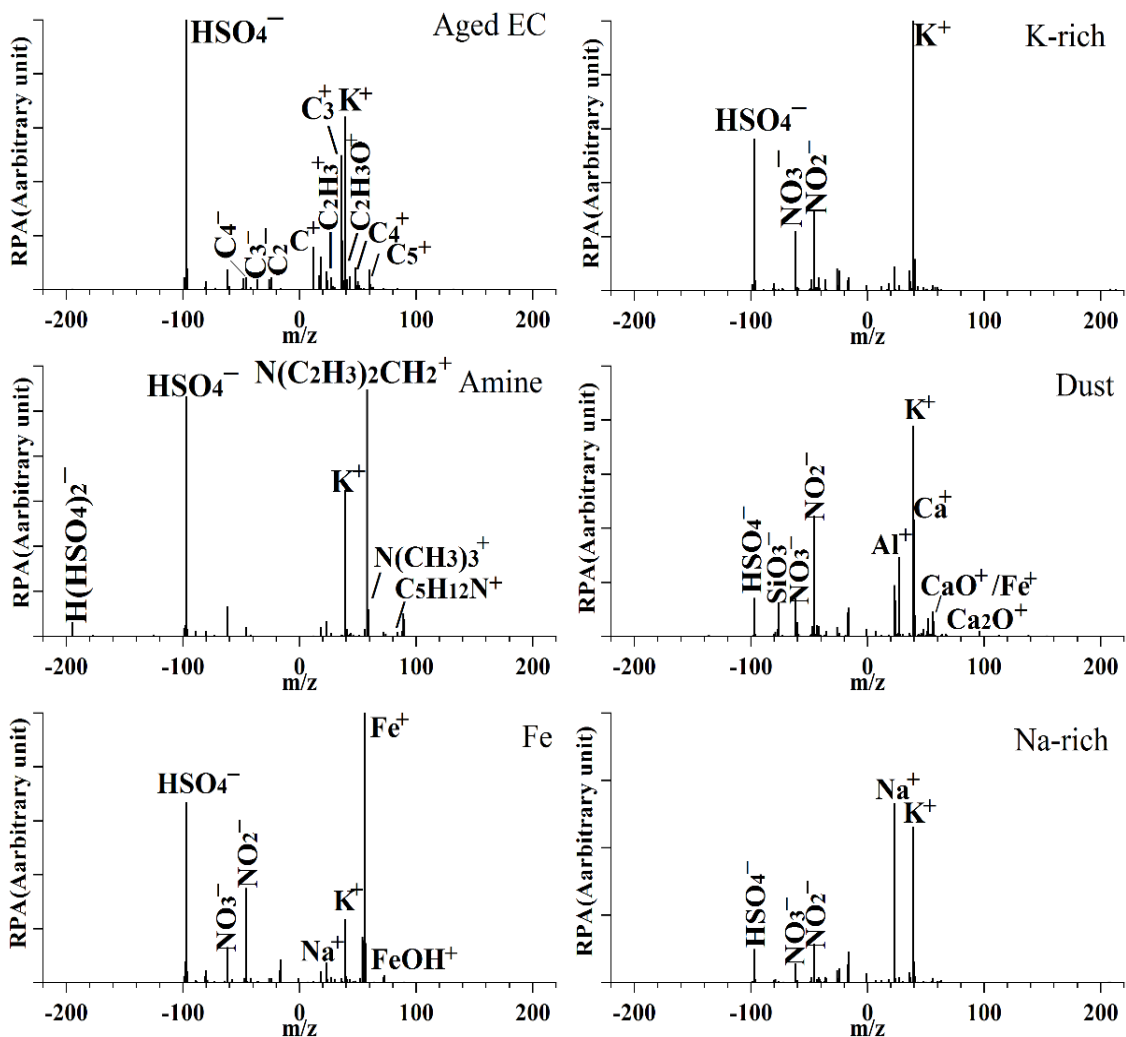
881

(b)



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883 Figure 2: (a) HYSPLIT back trajectories (72 h) for air masses at 1,800 m during the
 884 whole sampling period. The white borders and circle refer to the Pearl River Delta (city
 885 cluster 1) and Yangtze River Mid-Reaches city clusters (city cluster 2), respectively. **The**
 886 **fire date (yellow dots) are available at <https://earthdata.nasa.gov/>**;
 887 (b) Heights (above model ground) of the air masses as a function of time.



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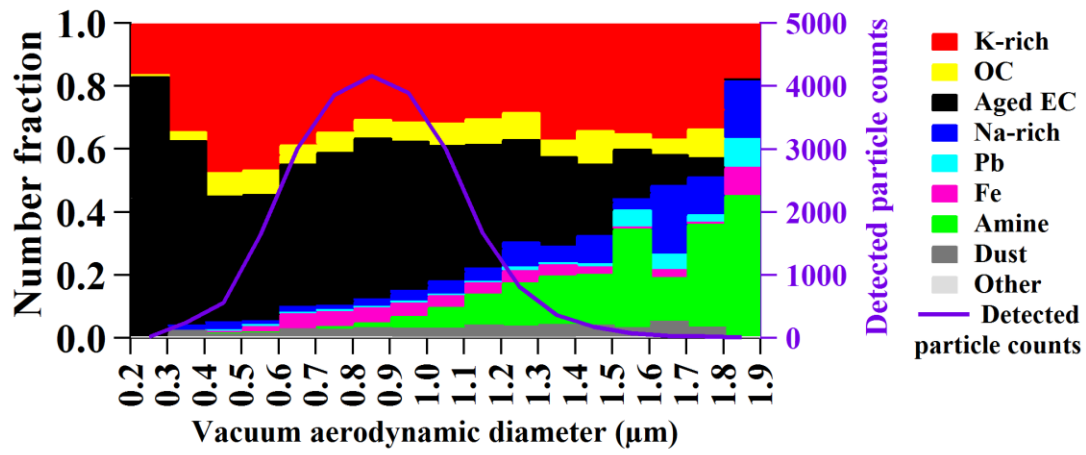
889

890 Figure 3: Averaged positive and negative mass spectra for the main 6 particle types

891 (Aged EC, K-rich, Amine, Dust, Fe, Na-rich) of the sampled particles. RPA in the

892 vertical axis refers to relative peak area. m/z in the horizontal axis represents mass-to-

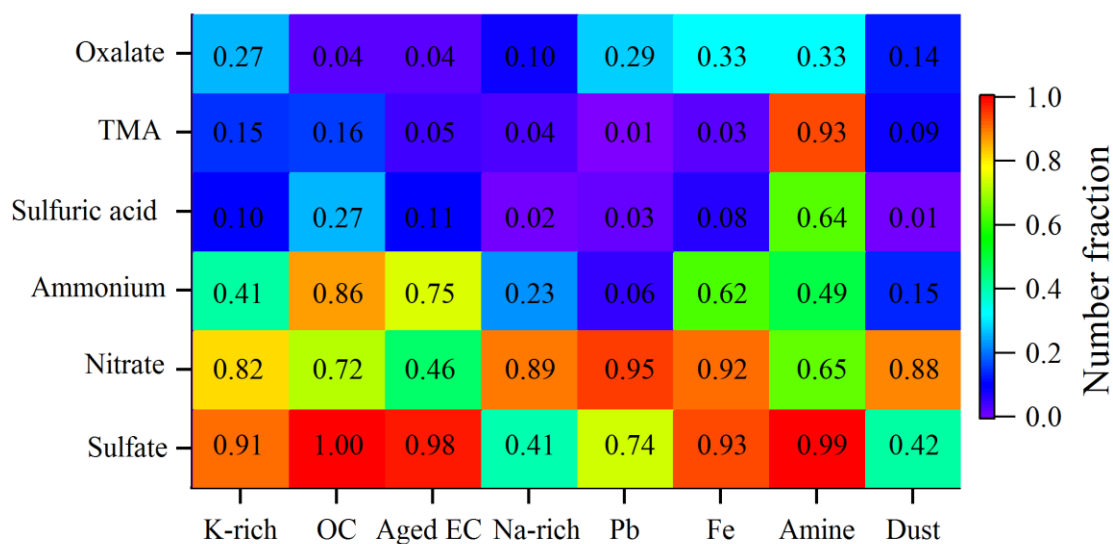
893 charge ratio.



894

895 Figure 4: Number fraction for size distribution of the cloud residual types in 100 nm size

896 intervals.



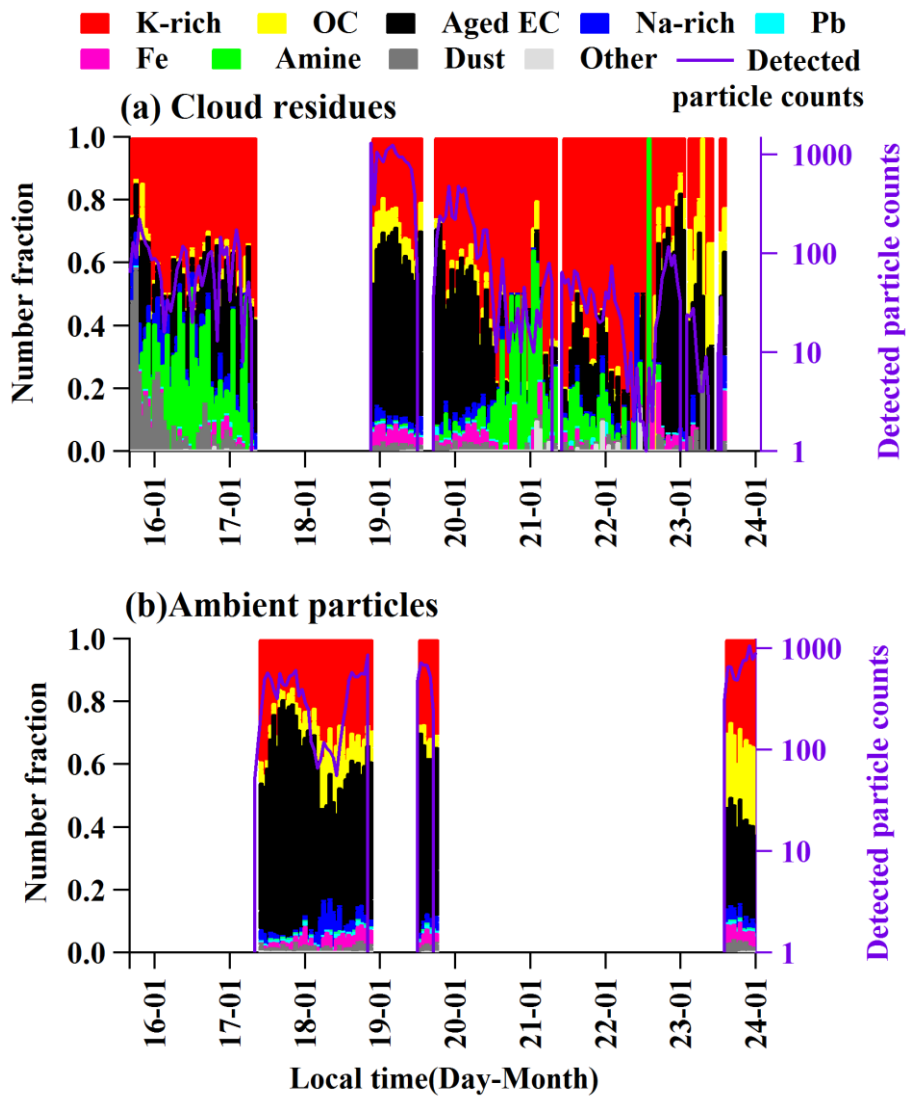
897

898 Figure 5: Number fraction of secondary markers associated with the total cloud residues

899 types; Sulfate (m/z , -97HSO_4^-), Nitrate (m/z , -46NO_2^- or -62NO_3^-), Ammonium (m/z ,

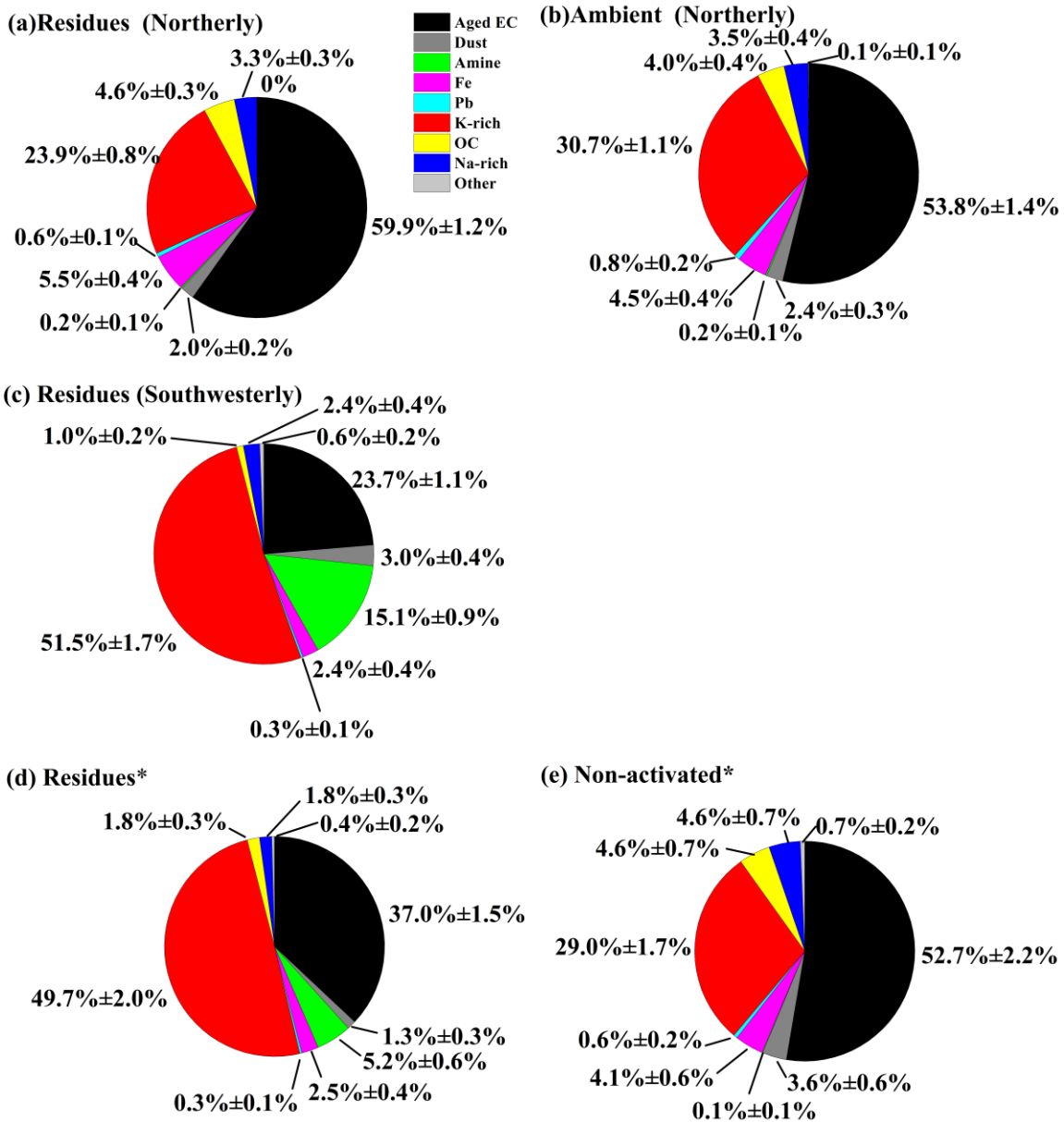
900 18NH_4^+), Sulfuric acid (m/z , $-195\text{H}(\text{HSO}_4)_2^-$), TMA (m/z , $59\text{N}(\text{CH}_3)_3^+$), Oxalate (m/z ,

901 $89\text{HC}_2\text{O}_4^-$).



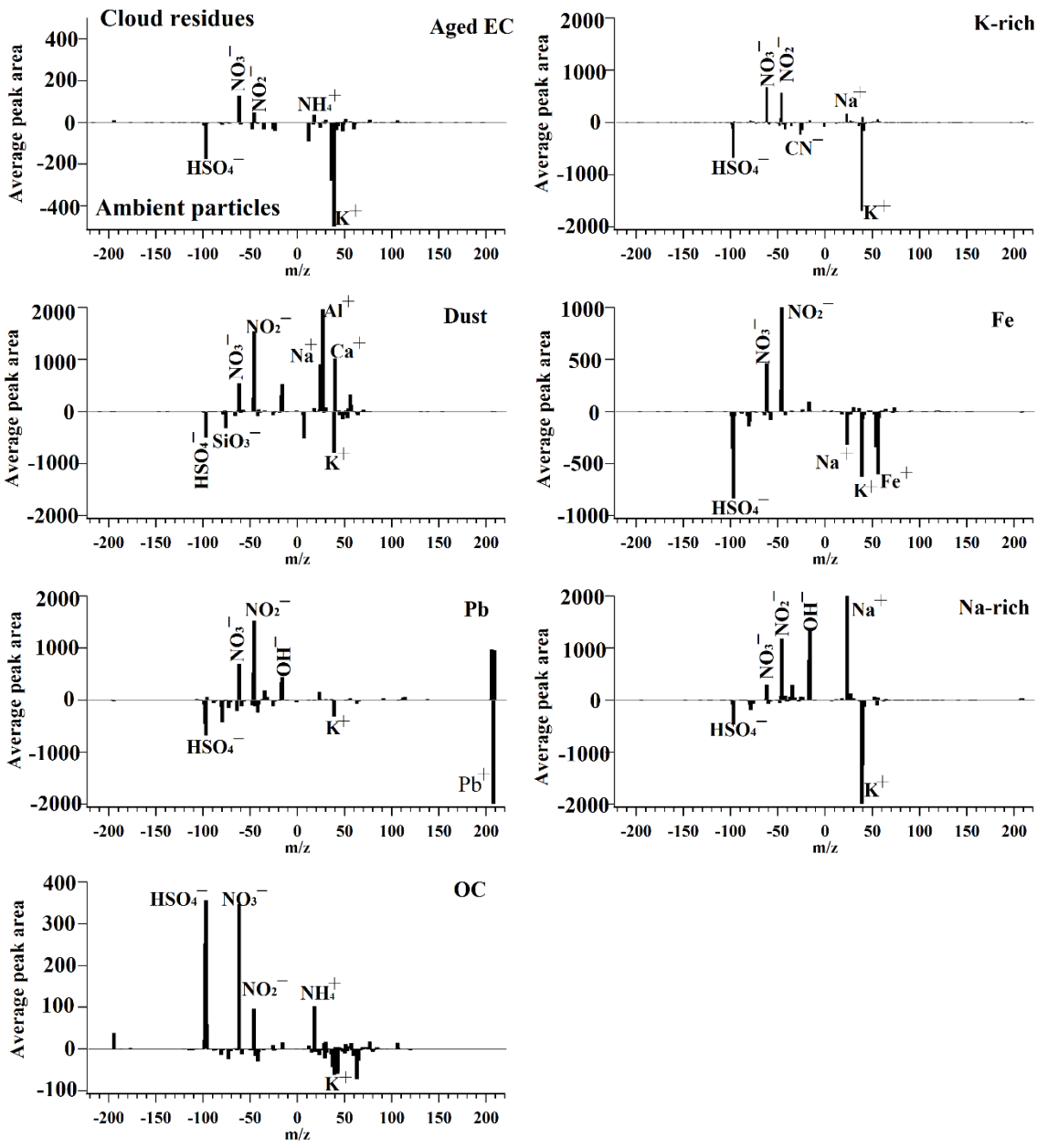
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Figure 6: The hourly average variations in the cloud residual and ambient particles during the whole sampling period.



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912

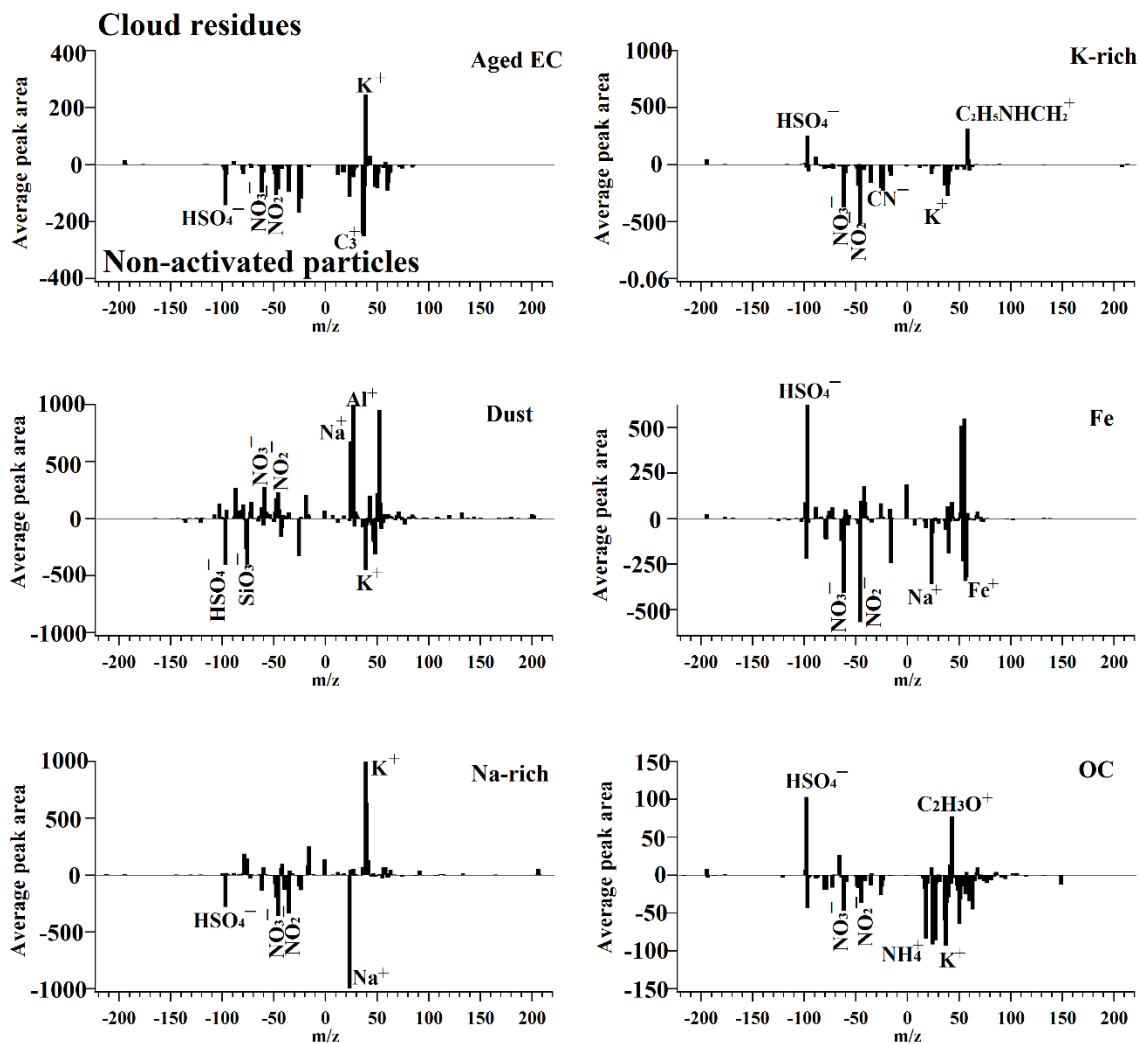
913 Figure 7: Number fraction of the cloud residues, ambient and non-activated particles. (a)
 914 cloud residues during northerly air mass; (b) ambient particle during northerly air mass;
 915 (c) cloud residues during southwesterly air mass; (d) cloud residues and (e) non-activated
 916 particles were alternately sampled with an interval of one hour during cloud III event.
 917 Uncertainties were calculated assuming Poisson statistics for analyzed particles.



918

919

920 Figure 8: Mass spectral subtraction plot of the average mass spectrum corresponding to
 921 cloud residues minus ambient particles. Positive area peaks correspond to higher
 922 abundance in cloud residues; whereas, negative area peaks show higher intensity in
 923 ambient particles.



924
925

926 Figure 9: Mass spectral subtraction plot of the average mass spectrum corresponding to
927 cloud residues minus non-activated particles. Positive area peaks correspond to higher
928 abundance in cloud residues; whereas, negative area peaks show higher intensity in non-
929 activated particles.