Response to comments

Manuscript Number: acp-2017-23

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

Summary and general comments

The authors present the results of online physico-chemical characterization of cloud residuals (>~8 μm in diameter), cloud particles (<2.5 μm da) and ambient particles (<2.5 μm 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 through 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 Li26-128: 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.

P7Li30-131: “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.

P7Li30-131: 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 (~20 μm) (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 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.

e 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. W 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 → 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 ~1 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 NH₃ 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.
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.

Oceans sound awkward.

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

Start a new paragraph.

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

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.

obtain the mixing state of individual ambient particles during

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

Their results showed...large particles

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

to 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.

They found an abundance of anthropogenic particles, including...

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

a mountain site in South China

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

Our measurements were carried out during...

We have corrected accordingly. Please refer to Line 118 of the revised manuscript.
This station is located at 200 km...

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

...(273 km2), where...

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

The ambient temperature

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

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.

Some → Previous

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

each single → single (or individual particles)

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

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.

Low levels of...exclude

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

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.

similar clusters, such as aged EC, ...

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

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

I suggest deleting two ‘and’s

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

Note that, on...

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

The word "big freeze" is a nomencreature 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.

the main six particle types

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

The strong K+ ion...

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

Awkward/incomplete sentence - I suggest rephrazing 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.

suffer from the bias related to...

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

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

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

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 Jungraujoch 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 fun 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, 18NH₄⁺) 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.
Thus, our data suggest that...
We have corrected accordingly. Please refer to Line 367 of the revised manuscript.

in two cloud residual types
We have corrected accordingly. Please refer to Line 364 of the revised manuscript.

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.

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.

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

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

...(Pratt et al., 2009). It may...
We have corrected accordingly. Please refer to Line 393 of the revised manuscript.

...is mainly based on...
We have corrected accordingly. Please refer to Line 396 of the revised manuscript.

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

...to the K-rich type and probably...
We have corrected accordingly. Please refer to Line 399 of the revised manuscript.

_P18L378:_ sensitive $\rightarrow$ 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 $\rightarrow$ 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.
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.

for both the...

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

This data implies...

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

...with one hour intervals. The ambient...

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

Thus, the data suggest that the initial...

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

cloudy air occurred around

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

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.

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.

showed that there were no significant changes

We have corrected accordingly. Please refer to Lines 485-486 of the revised manuscript.
as discussed in Sect. 3.3.

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

do not active as CCN → are not active as CCN

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

In comparing → When comparing

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

has been observed to account for → accounted for

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

the differences

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

when compared to

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

nitrate-containing

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

is most likely to be → possibly reflect the

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

confirmed that the update of gaseous HNO3 is an...

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

the increased nitrate level

We have corrected accordingly. Please refer to Lines 514-515 of the revised manuscript.
We have corrected accordingly. Please refer to Line 516 of the revised manuscript.

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

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

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

We have detected the sentence due to incomplete sentence.

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.

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

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

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


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

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**Highlights**

1. EC-containing particles were the largest fraction of the total cloud residues (49.3% by number), dominating in the range of 0.2-1.0 μm.

2. The Nf of the cloud residue types was influenced by air mass chemistry.

3. Amine particles represented from 0.2% to 15.1% by number of the total cloud residues when air masses changed from northerly to southwesterly.

4. Compared with non-activated particles, nitrate intensity decreased in cloud residues except dust type.
**Abstract**

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

Aerosol-cloud interactions influence the thermodynamic and radiation balance of the atmosphere (IPCC, Boucher et al., 2013). Anthropogenic particles can increase number concentration of small cloud droplets, and, in turn, affect reflectivity and life time of clouds (Stier et al., 2005; Lohmann et al., 2007; Rosenfeld et al., 2008). In situ cloud chemical measurements have shown varied chemical composition of cloud water or residues at various regions (Sorooshian et al., 2007a; Roth et al., 2016; Li et al., 2017).

Despite a large number of aerosol/cloud studies over the past 20 years, the uncertainty for evaluating radiative forcing due to aerosol-cloud interactions has not been reduced (Seinfeld et al., 2016). Therefore, it is crucial to assess how atmospheric aerosol particles contribute and interact with cloud droplets.

The ability of aerosol particles to act as cloud condensation nuclei (CCN) is dependent on the size and chemical composition of 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 affected 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.

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

Over the past three decades, China has undergone rapid economic growth accompanied by increased aerosol emissions. Although scientists have worked to increase our
understanding of an emissions inventory and the temporal and spatial variation of atmospheric aerosols in China (Zhang et al., 2012b), only few studies have employed direct observation of the chemical composition and mixing state of cloud/fog droplets. Li et al. (2011b) utilized transmission electron microscopy to obtain the mixing state of individual ambient particles during cloud events at Mt. Tai in northern China. This result showed that sulfate-related salts dominated in larger particles. Bi et al. (2016) used a ground-counterflow virtual impactor (GCVI) coupled with a real-time single particle aerosol mass spectrometer (SPAMS) to explore the chemical composition and mixing state of individual fog residual particles at ground level in an urban area of South China. They found an abundance of EC-containing particles in fog residues. Here, we present a study on the chemical composition and mixing state of individual cloud residue particles at a mountain site in South China. The same experimental methods of Bi et al. (2016) were used in this study. The size distribution, chemical composition and mixing state of cloud residues during cloud events are discussed. Moreover, the chemical compositions of ambient and non-activated particles were also compared with the cloud residues. The aim of this study is to assess the potential effects of anthropogenic aerosols from regional transportation on cloud formation and to investigate the dominant particle types in cloud droplets at a mountain site in South China.

2 Experimental

2.1 Measurement site

Our measurements were carried out during 15-26 Jan, 2016. The sampling site was located in the Nanling Background Station (112° 53’ 56” E, 24° 41’ 56” N, 1,690 m a.s.l.)
at the National Air Pollution Monitoring System in South China (Figure S1). This station is located at 200 km north of the metropolitan city Guangzhou and 350 km north of the South China Sea (Figure S1). This site is also surrounded by a national park forest (273 km²), where there are scarcely any emissions from anthropogenic activities. During the winter monsoon period, air pollution from northern China moves to southern China and crosses the study region (Lee et al., 2005).

2.2 Instrumentation

In this study, a GCVI inlet system (GCVI Model 1205, Brechtel Mfg. Inc.) was used to sample cloud droplets with a diameter greater than 8 µm. The ambient temperature on average was 6.9 °C (ranging from -7.2 to 11.4 °C) during cloud events. 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. The measurements of the droplet size spectra in this region performed during the winter of 1999-2001 showed that size of cloud droplets ranged from 4 to 25 µm with average size of 10 µm and a corresponding liquid water content of 0.11-0.15 g m⁻³ (Deng et al., 2007). Previous study in other mountain site also showed an average size at ~10 µm (Borys et al., 2000). Hence, assuming that size distribution of cloud droplets mostly was above 8 µm in this region, The sampled cloud droplets were passed through an evaporation chamber (air flow temperature at 40 °C), where the associated water was removed and the dry residue particles (with the air flow RH lower than 30%) remained. A stream of filtered and heated ambient air (counterflow) was provided by a compressor. The particle
transmission efficiency of the cut size (8 µm) was 50%. The enrichment factor of the particles collected by the GCVI inlet was estimated to be 5.25 based on theoretical calculation (Shingler et al., 2012). Ambient particles were collected through an ambient inlet with a cut-off aerodynamic diameter ($d_a$) of 2.5 µm when cloud-free periods were present. Non-activated (interstitial) particles were sampled through the ambient inlet during the cloud events in this study. The ambient or non-activated particles inlet was dried using a silica gel diffusion dryer. During cloud-free periods, a ratio of particle concentration measured behind the CVI (below 1 cm$^{-3}$) to ambient aerosol concentration (2,000 cm$^{-3}$) was 0.0005, indicating that instances of particle breakthrough and small particle contamination were absent.

The cloud droplet residues, ambient or non-activated particles were subsequently analyzed by a suite of aerosol measurement devices, including a SPAMS (Hexin Analytical Instrument Co., Ltd., Guangzhou, China), a scanning mobility particle sizer (SMPS) (MSP Cooperation) and an aethalometer (AE-33, Magee Scientific Inc.).

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

2.3 Definition of cloud events

To reliably identify the presence of cloud events, an upper-limit visibility threshold of 5 km and a lower-limit relative humidity (RH) threshold of 95% were set in the GCVI software (Bi et al., 2016). Three long-lasting cloud events occurred during the periods of 16:00 (local time) 15 Jan - 07:00 17 Jan (cloud I), 20:00 18 Jan - 12:00 19 Jan (cloud II) and 17:00 19 Jan - 13:00 23 Jan (cloud III), as marked in Figure 1. In addition, a cloud event occurred at 14:40 - 15:00 on 17 Jan, but we did not do an analysis due to the short duration. The measured cloud residual concentration was integrated by the SMPS and was then corrected by the enrichment factor and transmission efficiency of the GCVI. The corrected cloud residual concentrations on average were 436 cm\(^{-3}\), 568 cm\(^{-3}\) and 544 cm\(^{-3}\) for cloud I, cloud II and cloud III, respectively (Figure S2). From 10:00 21 Jan to 13:00 23 Jan, cloud residues and non-activated particles were alternately sampled with an interval of one hour. During this period, a ratio of number residues to total number particles (sum of cloud residues and non-activated particle) on average was 0.43±0.20. Low levels of PM\(_{2.5}\) (\(\sim 12.7\) µg m\(^{-3}\)) exclude the influence of hazy days. A rainfall detector of the GCVI system was also used to exclude rain droplet contamination. When cloud events occurred without precipitation, sampling was automatically triggered by the GCVI control software (Bi et al., 2016).
2.4 Particle classification

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

3 Results and discussion

3.1 Back trajectories and meteorological conditions

Back trajectories in this study were calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT Model). A height of the HYSPLIT model in the study region (a spatial resolution of 0.5° × 0.5°) is averaged 500 m a.s.l., lower than height of the observed site (1,690 m a.s.l.). Thus, a height of 1,800 m a.s.l. (approximately 100 m above the observed site) was chosen as an endpoint in the model. The station was mainly affected by southwesterly or northerly air masses in this study (Figure 2). In addition, the beginning altitude of the southwesterly air masses traversed at
lower heights relative to the northerly air masses (Figure 2). The southwesterly air masses, accompanied by *warm moist airflows*, occurred during 15-17 and 20-21 Jan, which promoted *high RH condition* (Figure 1). Conversely, the northerly air masses, associated with *cool dry airstreams*, occurred during 18 and 23-24 Jan and led to a decrease in temperature and relative humidity. Note that, on 18-19 and 22-23 Jan, the air mass encountered initial mixing of northerly cloud-free air and southwesterly cloudy air. Entrainment of nuclei particles originated from northern air masses might be activated to cloud droplets (Sect. 3.4).

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

3.2 The chemical characterization of cloud droplet residues

Figure 3 shows the average positive and negative mass spectra of the main six particle types. The Aged EC particles were characterized by EC cluster ions (e.g., m/z ±12C\(^{+/-}\), ±36C\(_3^{+/-}\), ±48C\(_4^{+/-}\), ±60C\(_5^{+/-}\), …) and a strong K\(^+\) ion signal (m/z 39K\(^+\)) as well as a
sulfate ion signal (m/z -97HSO$_4^-$), and some minor organic markers (m/z 27C$_2$H$_5^+$, 43C$_2$H$_3$O$^+$) (Moffet and Prather, 2009). EC particles mainly originated from combustion processes (Bond et al., 2013). The strong K$^+$ ion signal in the Aged EC particles implies partially originated from biomass burning sources (Bi et al. 2011). The Aged EC particle type was the largest fraction (49.3% by number) of the total cloud residues (Figure S3). In addition, number fraction (Nf) of the Aged EC residues significantly decreased from 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). Note that the chemical composition of cloud residues is dependent on the particle size (Roth et al., 2016), and the number reported for each particle type might suffer from the bias related to size-dependent transmission efficiency (Qin et al., 2006). The relative fraction of cloud residues in 0.1 μm size interval is presented to minimize the influence of size-dependent transmission efficiency of single particle mass spectrometry (Roth et al., 2016).

The K-rich particles exhibited the highest peak at m/z 39K$^+$, mainly combined with sulfate and nitrate (m/z -46NO$_2^-$, -62NO$_3^-$) and presumably derived from biomass/biofuel burning source (Moffet et al., 2008; Pratt et al. 2011; Zhang et al., 2013). An aged time of 81-88 min biomass burning particles were found to show an increase in the mass fractions of ammonium, sulfate, and nitrate (Pratt et al. 2011). In this study, the K-rich particles would be expected to experience aged process due to strong sulfate and nitrate signals (Hudson et al. 2004; Pratt et al. 2011). Aged biomass burning particles can participate in cloud droplets formation and show an effective CCN activity (Pratt et al. 2010a). The K-rich particle type, the second largest contributor, accounted for 33.9% by number of the total cloud residues (Figure S3).
The abundant aged soot/EC and biomass burning particles were often detected in cloud residues (Pratt et al., 2010a; Roth et al., 2016). The contribution of local anthropogenic origins to aged soot and/or biomass burning particles in cloud/fog residues has been reported in Schmücke (Roth et al., 2016) and Guangzhou city (Bi et al., 2016). At the North Slope of Alaska, the measurement of biomass burning particles in cloud residues mainly resulted from local vicinity or as far away as Siberia and Asian sources (Zelenyuk et al., 2010; Hiranuma et al., 2013). Similarly, the majority of Aged EC and K-rich cloud residues observed here are expected to originate from long-range transportation due to insignificant sources of local anthropogenic emissions and the fire dots (Figure 2). At the Jungfraujoch station (3,580 m a.s.l.) in Europe, the K-rich (biomass burning) particles only contributed 3% of the cloud droplets, and the Aged EC residuals were insignificant (<1% by number) (Kamphus et al., 2010). The Jungfraujoch station is predominantly within the free tropospheric condition, such that the biomass burning contribution can be expected to be lower than at other sites.

The Amine particles were characterized by related amine ion signals at m/z 58C₂H₅NHCH₃⁺ (diethylamine, DEA), 59N(CH₃)₃⁺ (trimethylamine, TMA) and 86C₅H₁₂N⁺ (triethylamine, TEA) (Angelino et al., 2001; Moffet et al., 2008). This particle type also contained sulfuric acid ion signals at m/z -195H(HSO₄)²⁻, indicative of acidic particles (Rehbein et al., 2011). The Amine particles represented 3.8% by number of the total cloud residues (Figure S3). Higher Nf of the Amine residues was detected in the size range from 0.7 to 1.9 μm relative to the size range from 0.2 to 0.6 μm (16.7% versus 0.4%), as shown in Figure 4. Aqueous reactions improving the participation of amine have been observed in Guangzhou (Zhang et al., 2012a) and Southern Ontario
A recent study also showed a clear enhancement of amine-containing particles in cloud residues compared to the ambient particles (9% versus 2% by number) (Roth et al., 2016). It indicates a preferential formation of amine within the cloud, which is in contrast to the observations of Bi et al. (2016). It might suggest 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).

The Dust particles presented significant ions at m/z 40Ca+, 56CaO/Fe+, 96Ca2O+ and -76SiO3− and sulfate as well as nitrate markers. Previous studies showed that dust particles that are internally mixed with sulfate and nitrate are expected to act as CCN (Twohy and Anderson 2008; Twohy et al., 2009), despite sulfate and nitrate partial formation from in-cloud production. This type contributed 2.9% by number of the total cloud residues (Figure S3). A slight increase in Nf of the Dust residues was observed in size range above 0.5 μm relative to that below 0.5 μm (3.0% versus 1.0% by number). At Mt. Tai in northern China, a high concentration of Ca2+ in cloud/fog water was mainly attributed to a sandstorm event during the spring season (Wang et al., 2011). At Mt. Heng in southern China, the abundant crust-related elements (e.g., Al) observed in cloud water is due to Asian dust storms that occurred in March-May (Li et al., 2017). Based on the backward trajectory, the site was unlikely affected by sandstorm source in northwestern China during the cloud events. Local dust emissions by anthropogenic-disturbing soils or removing vegetation cover can be excluded as a result of forest protection. Additionally, dust residues may have occupied larger CCN (Tang et al., 2016), which cannot be
detected by the SPAMS. Hence, a low fraction (2.9% by number) of dust cloud residue might be due to the limitation of the SPAMS.

The Fe particles had its typical ions at m/z 56Fe$^+$ and internally mixed with sulfate and nitrate, made up 4.1% by number of the total cloud residues. Approximately 16% of the Fe cloud residues contained Ca$^+$ peak (m/z 40). Predominant Fe ion peaks possibly indicates the contribution from anthropogenic sources (Zhang et al., 2014), especially the northern air masses across iron/steel industrial activities in Yangtze River Mid-Reaches city clusters (Figure 2). The contribution of anthropogenic and natural Fe-containing particles sources (Moteki et al., 2017) to observed Fe-containing residues is expected. The presence of Fe in the cloud droplets play an important role in aqueous-phase SO$_2$ catalytic oxidation in cloud processing (Harris et al., 2013), thus accelerating the sulfate content of Fe-containing particles in cloud processing.

The Na-rich particles were mainly composed of ion peaks at m/z 23Na$^+$ and 39K$^+$ in the positive mass spectra, and nitrate and sulfate species in the negative mass spectra, made up 3.0% by number of the total cloud residues. Na-rich particles are formed from varied sources including industrial emissions, sea salt or dry lake beds (Moffet et al. 2008). The Nf of 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). However, the related sea salt ion peak area (m/z, 81/83 Na$_2$$^{35}$Cl$^+$/Na$_2$$^{37}$Cl$^+$) were enhanced for Na-rich particles origination from maritime air mass relative to continental air mass (3.8 ± 2.4 times). The continental air masses crossed industrial areas where the Yangtze River Mid-Reaches city cluster is located (Figure 2). Industrial emissions were a possible contributor to Na-rich particles under the influence of continental air masses.
This might suggest that the Na-rich particles were originated from both industrial emissions and sea salts.

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

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

The high Nfs of sulfate-containing particles were found in the K-rich (91%), OC (100%), Aged EC (98%), Pb (74%), Fe (93%) and Amine (99%) cloud residues, as shown in Figure 5. Lower Nfs of sulfate-containing particles were observed in the Na-rich (41%) and Dust (42%) cloud residues. In contrast, nitrate-containing particles contributed 89% and 88% by number to the Na-rich and Dust cloud residues, respectively. The acid displacement reaction of sea salt chloride (Na-rich particles) by HNO₃ might lead to a depletion of chloride and enhancement of nitrate (Laskin et al., 2012). Similarly, the heterogeneous chemistry of HNO₃ in the dust particles also contributes the preferential enrichment of nitrate (Tang et al., 2016). Moreover, after activation, uptake of gas-phase HNO₃ would increase nitrate level in the cloud residues (Schneider et al., 2017). The nitrate in the cloud residues was thought to be in the form of ammonium nitrate by estimating the ratio of m/z 30 to m/z 46 in AMS data (Drewnick et al., 2007; Hayden et al., 2008). 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 two cloud residual types. The Na-rich and Dust types were mainly composed of alkaline ion peaks (m/z, 23Na⁺, 39K⁺ and 40Ca⁺) in position mass spectra (Figure 3), accompanied with larger fraction (88-89%) of nitrate. Thus, our data suggests that nitrate might exist in the form of Ca(NO₃)₂, NaNO₃ or KNO₃ in the Dust and Na-rich cloud residues. It should be noted that the evaporation chamber of the GCVI may lead to a reduction of ammonium nitrate in the cloud residues (Hayden et al., 2008). 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. Previous field studies have found that Aged EC (soot) fog/cloud residues are mainly internally mixed with sulfate (Pratt et al., 2010a; Harris et al., 2014; Bi et al., 2016). Aged EC particles mixed with sulfate are good CCN, rather than formed by in-cloud processing (Bi et al., 2016; Roth et al., 2016). Laboratory measurements have also demonstrated that EC particles internally mixed with sulfate showed a high hygroscopic behavior and thus affect CCN ability (McMeeking et al., 2011). High portions (75-86% by number) of ammonium-containing particles were observed for the OC and Aged EC cloud residues, suggesting that ammonium will mostly be in the form of ammonium sulfate or ammonium nitrate for two cloud residual types (Zhang et al., 2017). This result also implies that ammonium-containing particles are preferentially activated or enhanced uptake of gaseous NH₃ to neutralize acidic cloud droplets for the OC and EC types.

Water soluble organics (e.g., amine and oxalate) have previously been measured in cloud water/residues (Sellegri et al., 2003b; Sorooshian et al., 2007a; Pratt et al., 2010a). The presence of TMA (93% by number) in the Amine cloud residues is expected to promote water uptake activity (Sorooshian et al., 2007b). A total of 3,410 oxalate-containing particles (m/z, -89HC₂O₄⁻) represented 14.4% by number of the total cloud residues, which was mainly associated with the K-rich cloud residues (~70% by number). Oxalate-containing particles (~30% by number) in the metal (Pb, Fe) cloud residues might be in the form of metal oxalate complexes from reactions of in-cloud formation oxalate with metals (Furukawa and Takahashi, 2011). Oxalate can readily partition into the particle phase to form amine salts (Pratt et al., 2009b). It may facilitate the entrainment of oxalate (33% by number) in the Amine residues. A low fraction (4%) of
oxalate-containing particles in the OC type is a result of restrictive classification. Classification of the OC particles is mainly based on intense organic carbon ion signals (e.g., m/z 27C$_2$H$_5^+$, 37C$_3$H$_7^+$, 43C$_3$H$_3$O$^+$ and 51C$_4$H$_5^+$). The majority of oxalate-containing particles were internally mixed with the K-rich type. Therefore, oxalate was classified to the K-rich type and probably contributed from biomass burning. The K-rich particles could contain an abundant of organics (Pratt et al. 2011), however, the signals of organics were covered by the potassium due to its high sensitivity to the laser.

3.4 Comparison of cloud residues in different air mass sources

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

The ambient RH increased from 60% at 19:00 to nearly 100% at 21:00 on 18 Jan (Figure 1). The ambient temperature also increased from 1.3 °C at 22:00 on 18 Jan to 3.2 °C at 06:00 on 19 Jan (Figure 1). These changes imply that the air mass changed from northerly cloud-free air to southwesterly cloudy air at night on 18 Jan (Figure 2).
18-19 Jan, the cloud residues and ambient particles showed similar chemical characteristics and were dominated by Aged EC particles (Figure 6). A lack of significant variation in the particle types for this period suggests that nuclei particles originated from northerly cloud-free air could be activated to become cloud droplets. When a cloud-free event occurred at 11:00-17:00 on 19 Jan, ambient particles remained a high level of PM$_{2.5}$ ($\sim 22.7$ μg m$^{-3}$). The southwesterly wind flow on 19-20 Jan was too weak ($\sim 2.75$ m s$^{-1}$) to dilute particles originated from the northerly air masses (Figure 1). Additionally, a high RH (90%) air mass at height 1,500 m (a.s.l.) gradually moved to northern China from 19 to 20 Jan (Figure S5). These changes might have led to similar residual particle types observed from 19 Jan to 20 Jan, although the site encountered southwesterly cloudy air on 19-20 Jan (Figure 2).

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

The K-rich type was found to contribute 23.9% to the cloud residues in the northerly air mass, which was significantly lower than its contribution to the southwesterly air mass (51.5%), as shown in Figure 7. A similarity in averaged mass spectrum of the K-rich
residues was found for the southwesterly and northerly air masses (Figure S6). The considerable increase of K-rich cloud residues suggests a major influence of regional biomass-burning activities. Biomass-burning emissions from Southeast Asia, including Myanmar, Vietnam, Laos and Thailand, where abundant fire dots are observed (Figure 2), could have been transported to the sampling site under a southwesterly air mass (Duncan et al., 2003). In contrast, the Aged EC type represented only 23.7% of the cloud residues under the influence of the southwesterly air mass, which was significantly lower than observations for the northerly air mass (59.9%), as shown in Figure 7. This result suggests that the northern air mass has a greater influence on the presence of Aged EC cloud residues.

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

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

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

The cloud residues and non-activated particles were alternately sampled with an interval of one hour from 21 Jan to 23 Jan. The ambient temperature decreased from 6 °C at 11:00 to 0 °C at 23:00 on 22 Jan (Figure 1). Ambient particles level (sum of residual and non-activated particles) showed a clearly increase from 156 cm⁻³ to 1460 cm⁻³ during this period (Figure S2). Thus, the data suggests that the initial mixing of northerly cloud-free air and southwesterly cloudy air occurred around noon on 22 Jan. 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) (Mertes et al., 2005; Kleinman et al., 2012; Hammer et al., 2014), which can be detected by the SPAMS.

The contribution of K-rich particles in cloud residues (23.9%) slightly decreased relative to ambient particles (30.7%), as shown in Figure 7. Previous studies have found
that there were no significant changes in Nf of biomass-burning particles for cloud residues relative to ambient particles (Pratt et al., 2010a; Roth et al., 2016). The biomass-burning particles internally mixed with soluble species (e.g., sulfate, nitrate and oxalate) enhanced their ability to act as CCN, as discussed in Sect. 3.3. Kamphus et al. (2010) reported that biomass-burning particles account for only 3% of cloud residues compared with 43% of ambient particles, and they suspected that biomass-burning particles might exist in the form of tar balls (hydrophobic materials). A slight increase in Nf of the Aged EC cloud residues (59.9%) was observed relative to ambient particles (53.8%), as shown in Figure 7. In general, freshly emitted EC particles are less hydrophilic and are not active as CCN (Bond et al., 2013). The Aged EC particles show a high degree of internal mixing with secondary inorganic compounds in this study (Figure 5), improving their ability to act as CCN. The remaining particle types showed no clear differences in Nf between cloud residues and ambient particles.

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

Figure 8 and 9 show the differences in average mass spectra for cloud residues versus ambient particles, as well as cloud residues versus non-activated particles, respectively. Nitrate intensity (average ion peak area) enhanced in the cloud residues when compared to ambient particles. In addition, nitrate-containing particles accounted
for 70% of the cloud residues compared to 38% of the ambient particles. Drewnick et al. (2007) suggested that rather than sulfate, high nitrate content in pre-existing particles preferentially acted as cloud droplets. Compared with nitrate-containing ambient particles, larger size of containing-nitrate residues (Figure S8) possibly reflect the uptake of gaseous HNO₃ during cloud process (Hayden et al. 2008; Roth et al., 2016). A recent study also confirmed that the update of gaseous HNO₃ is an important contributor for the increased nitrate level in the cloud residuals (Schneider et al., 2017). Interestingly, we observed a decrease in nitrate intensity in cloud residues except dust type (Figure 9), and a large size distribution of nitrate-containing cloud residues (Figure S7) when compared with non-activated particles. This result suggests that particle size, rather than nitrate content, plays a more important role in the activation of particles into cloud droplets.

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

The in-cloud process has been reported to be an important pathway for the production of amine particles (Rehbein et al., 2011; Zhang et al., 2012a). In this study, no remarkable change in Nf of the Amine cloud residues was obtained relative to the
ambient particles (0.2% versus 0.2% by number), as shown in Figure 7. The absence of amine species in cloud residues may be partially affected by droplet evaporation in the GCVI (Bi et al., 2016). However, there was a high fraction of the amine cloud residuals when the southwesterly air mass prevailed, as discussed in Sect. 3.4. A lack of gas-phase amines may be the cause of few amine particles detected in the ambient particles and cloud residues (Rehbein et al., 2011). An increase in Nf of cloud residues was observed compared with non-activated particles (5.2% versus 0.1% by number), as shown in Figure 7. An increase of particle water content facilitates partitioning of gas-phase amine species into the aqueous phase when gas-phase amines present (Rehbein et al., 2011).

4 Conclusions

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

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References


Figure 1: The hourly average variations in meteorological conditions (temperature, relative humidity, visibility, pressure, wind speed and direction) and PM$_{2.5}$. 
Figure 2: (a) HYSPLIT back trajectories (72 h) for air masses at 1,800 m during the whole sampling period. The white borders and circle refer to the Pearl River Delta (city cluster 1) and Yangtze River Mid-Reaches city clusters (city cluster 2), respectively. The fire date (yellow dots) are available at https://earthdata.nasa.gov/; (b) Heights (above model ground) of the air masses as a function of time.
Figure 3: Averaged positive and negative mass spectra for the main 6 particle types (Aged EC, K-rich, Amine, Dust, Fe, Na-rich) of the sampled particles. RPA in the vertical axis refers to relative peak area. m/z in the horizontal axis represents mass-to-charge ratio.
Figure 4: Number fraction for size distribution of the cloud residual types in 100 nm size intervals.
Figure 5: Number fraction of secondary markers associated with the total cloud residues types; Sulfate (m/z, -97HSO\textsubscript{4}^-), Nitrate (m/z, -46NO\textsubscript{2}^- or -62NO\textsubscript{3}^-), Ammonium (m/z, 18NH\textsubscript{4}^+), Sulfuric acid (m/z, -195H(HSO\textsubscript{4})\textsubscript{2}^-), TMA (m/z, 59N(CH\textsubscript{3})\textsubscript{3}^+), Oxalate (m/z, -89HC\textsubscript{2}O\textsubscript{4}^-).
Figure 6: The hourly average variations in the cloud residual and ambient particles during the whole sampling period.
Figure 7: Number fraction of the cloud residues, ambient and non-activated particles. (a) cloud residues during northerly air mass; (b) ambient particle during northerly air mass; (c) cloud residues during southwesterly air mass; (d) cloud residues and (e) non-activated particles were alternately sampled with an interval of one hour during cloud III event. Uncertainties were calculated assuming Poisson statistics for analyzed particles.
Figure 8: Mass spectral subtraction plot of the average mass spectrum corresponding to cloud residues minus ambient particles. Positive area peaks correspond to higher abundance in cloud residues; whereas, negative area peaks show higher intensity in ambient particles.
Figure 9: Mass spectral subtraction plot of the average mass spectrum corresponding to cloud residues minus non-activated particles. Positive area peaks correspond to higher abundance in cloud residues, whereas, negative area peaks show higher intensity in non-activated particles.