Response to comments

Anonymous Referee #2

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This paper presents aerosol particle mixing state measurements and analysis of black carbon containing cloud drop residuals obtained during a 10 day campaign from a ground station at a remote mountain site located in southern China. Cloud droplet residual particles were sampled with a ground based CVI operating behind a compact wind tunnel and analyzed with a SP-AMS, SMPS, and an aethalometer. Drivers for activation, including residual composition and particle size, are investigated. Results are compared with concurrent cloud-free and interstitial aerosol particle sampling.

General comments:
This paper seems to be portrayed as an in-depth study on particle mixing state and the influence of mixing state and anthropogenic activities on CCN activity; however, it may be more accurately described as an individual case study, looking at three cloud events in a single location. Care should be taken not to over-emphasize the implications of these results to all aspects of cloud activation processes. Support qualitative statements throughout the paper with quantitative results.

We would like to thank the reviewer for his/her useful comments and recommendations to improve the manuscript.

We agree with the comment that it is more accurately described as an individual case study. We have revised the title to "The single-particle mixing state and cloud scavenging of black carbon: a case study at a high-altitude mountain site in southern

China". We also attempt to support qualitative statements throughout the paper with quantitative or semi-quantitative results as suggested. Please refer to the response to the specific comments as follows.

Specific comments:

Line 23-24: Other references have looked at the mixing state of BC particles in China. (e.g., Cheng et al. 2006; Wang et al., 2014). You have also referenced mixing state measurements by Huang et al. (2011) in Figure S7. You also reference another report of scavenging of BC particles made in China (Lines 70-72; Zhou et al., 2009)

We agree with the comment that mixing state and scavenging of BC particles have been previously investigated in China. In this study, we first attempted to link the cloud scavenging efficiency of BC particles directly with their mixing state in China. We thus revised the sentence to "In situ investigation on the cloud scavenging of BC in company with the mixing state was first reported in China" to make it clear. Please refer to Lines 23-24 of the revised manuscript.

Line 25-26: Please clarify or quantify the use of 'same extent'. Are you saying that the number fraction of particles containing black carbon is the same between 'cloud RES', 'cloud INT', and 'cloud free'?

Thanks for the comment. We have revised the sentence to "The number fraction of scavenged BC-containing particles is close to that of all the measured particles."

Line 27-28: This statement seems to contradict the previous (Line 25-26).

Thanks for the comment. As we discussed in Supplement Lines 126-128, it is attributed to two reasons: (1) BC-OC-sul particles only accounted for ~20% of BC-containing

particles, and (2) the other particles also contained OC-dominated particles (~10%).

Line 46: A number of studies have previously reported black carbon measurements in the free troposphere (e.g., Schwarz et al., 2013; Pusechel et al., 1992; Pósfai et al., 1999; Babu et al., 2011; Liu et al., 2010)

We agree with the comment that several studies have previously reported black carbon measurements in the free troposphere. However, simultaneous measurements on the mixing state and cloud scavenging of BC are still rare. We have revised the sentence to "Our results would improve the knowledge on the concentration, mixing state, and cloud scavenging of BC in the free troposphere." to clarify the statement.

Line 48: Please expand on the usability of these results in modeling studies.

Thanks for the comment. Our results on the concentration and cloud scavenging of BC could be used as a reference to compare with the modeling results, with respect to the southern China. As stated in the previous response, we have revised the sentence to "Our results would improve the knowledge on the concentration, mixing state, and cloud scavenging of BC in the free troposphere." to clarify the statement.

Line 50: Change 'residues' to 'residuals' for consistency.

It has been revised to "residual particles" accordingly.

Line 55: Fresh soot particles are generally very hydrophobic and generate organic layers over time, decreasing their hydrophobicity. Per your reference: "While freshly emitted soot is extremely hydrophobic, oxidation during aging causes soot to become more hydrophilic." (Zuberi et al., 2005)

Thanks for the comment. We have corrected “hydrophilic” to “hydrophobic”, and thus sentence was revised to “Fresh BC-containing particles are generally hydrophobic due to the presence of thin coatings of inorganic or organic materials (Zuberi et al., 2005), and during transport they become more hydrophilic when further coated through coagulation, condensation and photochemical oxidation (Zuberi et al., 2005; Zaveri et al., 2010; Matsui, 2016).”.

Line 60-61: This seems to contradict your statement in the abstract that “…measured BC-containing particles… were activated into cloud droplets to the same extent as all the measured particles”

Thanks for the comment. As we stated in the above response, freshly emitted BC particles are extremely hydrophobic, atmospheric aging (e.g., through coagulation, condensation and photochemical oxidation) causes them to become more hydrophilic. The in-cloud scavenging of BC should be enhanced to some extent, may be to the same extent as other aerosol compositions. Therefore, it does not contradict the statement in the abstract.

Line 72: Change ‘residues’ to ‘residuals’ for consistency.

It has been revised to “residual particles” accordingly.

Line 74: Change ‘would be altered’ to ‘could be altered’.

It has been changed as suggested.

Line 90: Change ‘residues’ to ‘residuals’ for consistency.

It has been revised to “residual particles” accordingly.

Line 112-116: What is the average boundary layer height compared to the surrounding ground altitude for this region? How frequently is this site sampling free tropospheric air?

Thanks for the comment. The average boundary layer height over the study compared to the surrounding ground altitude for this region is ~280 m, with the highest boundary layer height at ~1000 m. Regarding that the average surrounding ground altitude is ~500 m, it is reasonable to consider this site sampling free tropospheric air throughout the study. It is noted the boundary layer height was not measured over the study, instead, it is calculated from https://www.arl.noaa.gov. This information has been added in the revised manuscript, please refer to Lines 116-119.

Line 115: Change ‘isolated’ to ‘distant’ (indicate that it is not near any anthropogenic sources).

It has been changed as suggested.

Line 120: What is the particle size transmission efficiency for this wind tunnel set up? Are larger droplets transmitted through the tunnel with the same efficiency as smaller droplets?

Generally, the transmission efficiency of the droplets increased with increasing size, with 50% transmission efficiency at 8 μm. The detail information on the design and testing on the size-resolved transmission efficiency of the CVI inlet can be available elsewhere (Shingler et al., 2012). The inlet cut size was set to be 8 μm, at which the

transmission efficiency of droplets is 50%. This information has been added in the sampling setup, please refer to Lines 126-129 of the revised manuscript.

Line 121: What is the wind tunnel velocity used for the ground based setup? Was it ~80 m/s? You've reported an enhancement factor of 5.25 (Line 138), which would require a free stream velocity of ~80 m/s at 15 LPM sample flow in the BMI CVI.

The wind tunnel velocity used in this study is ~80 m/s. As suggested by the reviewer in the following comments, we have added this information in the revised manuscript as "A_{tip} is 1.67×10^{-5} m^2, q_{sample} is 15 l min^{-1}, and V_{air} was set to be ~80 m/s, coincides with an EF of 5.25.", please refer to Lines 129-133.

Line 127: Change "...particles that are capable of acting as CCN" to "...particles that were CCN"

It has been changed as suggested.

Line 127-128: Please clarify what you mean by "A testing before measurements demonstrates that the influence of background aerosols on the collection of cloud droplets could be negligible..."

Thanks for the comment. To make it clear, we have changed the sentence to "The influence of background particles on the collection of the cloud RES particles could be negligible. A test on the cloud-free air showed that the average particles number concentration sampled by the GCVI was ~1 cm^{-3}, far below the level ~2000 cm^{-3} in the cloud free air over the study (Zhang et al., 2017).".

Line 133-136: Please provide further information on the GCVI measurement

capabilities (visibility and rainfall detection). How are these measured by the instrument?

Thanks for the comment. We have added "The GCVI includes various sensors to monitor the temperature/RH, visibility (http://belfortinstrument.com/products/all-environment-visibility-sensor/), and rainfall/snow (http://www.meltyourice.com/products/controllers/ds-82/). The integrated rainfall/snow sensor helps to exclude sampling during rainy periods." in the Supplement, please refer to Lines 78-82.

*Line 137-139: Please change the following: "The enhancement factor (EF) for the particles collected by the GCVI is 5.25 (Shingler et al., 2012)" to indicate that the enhancement factor (EF) for the particles collected by the GCVI is calculated as EF = Atip*Vair/qsample, where this results in an EF for your setup of 5.25 using your wind tunnel velocity and your sample flow rate.*

We agree with the comment. We have changed these sentences to "The enhancement factor (EF) was calculated according to the equation (Shingler et al., 2012): EF = A_{tip}*V_{air}/q_{sample}, where A_{tip} is the area of the inlet tip where drops enter, V_{air} is wind tunnel velocity, and q_{sample} is the volumetric flow rate of sampled air in the CVI inlet. A_{tip} is 1.67×10^{-5} m^2, q_{sample} is 15 l min^{-1}, and V_{air} was set to be ~80 m/s, coincides with an EF of 5.25." in Lines 129-133 of the revised manuscript.

Line 140-149: Please provide uncertainties and detection limits for your instrument measurements or references for where this information can be found (state that this information is in the supporting information if necessary). Please provide total size range and bin resolution information for the SMPS instruments.

Thanks for the comment. The information on the uncertainties and detection limits of

our instrument measurements has been added in the Supplement as suggested. We also provided the information on the total size range and bin resolution for the SMPS instruments.

The detection limit for EBC measurements is < 10 ng m^{-3} with uncertainty at ~2 ng m^{-3} at the time-base of 1 minute. TEOM (https://www.thermofisher.com) measures the mass concentration of aerosol with the detection limited of ~100 ng m^{-3}, with an accuracy of ±0.75%. MSP SMPS (https://www.mspcorp.com) measures the number-based size distribution of particles ranged between 10-1000 nm in 48 size bins, with a detection limit of ~1 cm^{-3}, and an accuracy of ±10%. Grimm SMPS (https://www.mspcorp.com) measures the number-based size distribution of particles ranged between 10-1100 nm in 44 size bins, with a detection limit of ~1 cm^{-3}, and an accuracy of ±5%. The accuracy for the particle size measured by the SPAMS is within ±10%. Please refer to Lines 31, 55-57, and 82-89 of the revised Supplement.

Line 143: Change 'scan' to 'scanning'.

It has been changed as suggested.

Line 163: What MAC values were used to convert to EBC concentrations?

We have added the MAC values and the corresponding references for where the values are suggested. The sentence has been revised to "For AE–31, a specific attenuation cross-section σ_{ATN} of 16.6 m^2 g^{-1}, recommended by the manufacturer, was applied to calculate the EBC concentration with the equation: EBC = b_{ATN}/σ_{ATN}, where b_{ATN} is the optical attenuation coefficient. For AE-33, the ATN was converted to an EBC concentration using the mass absorption cross section of 7.77 m^2 g^{-1} according to the method recommended by Drinovec et al. (2015).". Please refer to Lines 44-48 of the revised Supplement.

Line 213: Change 'approximate' to 'approximately'.

It has been changed as suggested.

Line 216-218: This is a single event (Cloud II) and more sampling should be conducted to support this claim.

We agree with the comment. The mass concentration of EBC during Cloud II was approximately 200 ng m^{-3}, which is four times that (~50 ng m^{-3}) observed during the other two events. It is attributable to the strong impact of the northeastern air mass (Lin et al., 2017). We have clarified that this is a case study in the revised manuscript and revised the statement to "This case might provide partial evidence for the influence of anthropogenic emissions and atmospheric transport on the formation of clouds at the remote high-altitude site in southern China.", please refer to Line 222-224 of the revised manuscript.

Line 225-227: Do these percentages indicate the number of total particles that had detectable amounts of these individual components?

Thanks for the comment. These percentages indicate the number of total particles that had detectable amounts of these individual components. We have added "Y-axis indicates the number fraction of total particles that had detectable amounts of these individual ion peaks." to Fig. S3 to make it clear.

Line 247-261: There are many qualitative statements in this section that would benefit from supporting quantitative results (e.g., "…the enhancement was more obvious...", "…particles have been broadly observed…", "An abundance of BC-coated

materials…", etc..)

We agree with the comment. An adaptive resonance theory-based neural network algorithm (ART-2a) (Song et al., 1999) was applied to cluster the individual particles, based on the presence and intensities of ion peaks. The generated particle clusters were further manually grouped and three BC particle types were obtained. Therefore, the cut-point for categorizing a particle as "more intense sulfate" and "abundance of both sulfate and organics" is based on the intensities of sulfate and organics. To make it clear, we have shown the statistical analysis on the ion peak ratio of OC to BC and the average mass spectra for the BC types. More intense sulfate (RPA = ~0.3) was found for BC-sul2 and BC-OC-sul, relative to that (RPA = ~0.15) for BC-sul1 type. More abundance of OC was found for BC-OC-sul, the mean peak area ratio OC/BC of which is ~1, higher than those (< 0.3) for other BC types. Please refer to revised Fig. S2.

Line 259-260: Please explain this sentence, or link it to the previous study.

Thanks for the comment. This sentence has been revised to "Although an abundance of BC-coated materials was also observed at Mt. Soledad by a single particle soot photometer (Schroder et al., 2015), the chemical compositions of the coated materials cannot be obtained to provide further information on the mixing state of BC." to make it clear, as also commented by the Referee 1#. Please refer to Lines 262-266 of the revised manuscript.

Line 370: Was LWC measured during this study?

Thanks for the comment. LWC was not measured in the present study. We proposed the possible range of LWC through the comparison of number fraction of scavenged particles with previous studies. As shown in Lines 319-328, relatively lower

scavenging efficiency in the present study was most likely attributed to less dense clouds (with a liquid water content or LWC < 0.1 g m^{-3}). Generally, the half activated diameter increases with decreasing LWC. Henning et al. (2002) stated that particles with d_{ve} = 700 nm were only half activated with LWC < 0.1 g m^{-3}, in contrast, particles with d_{ve} = ~100 nm can be half activated when the LWC > 0.15 g m^{-3}. Similarly, Hammer et al. (2014) showed that only particles with a d_{ve} larger than 300 - 500 nm could be activated under low-LWC conditions (LWC < 0.1 g m^{-3}), which is a typical condition for the formation of fog at the ground level.

Figure captions: Refrain from including discussion and references in the figure captions (keep this in the text body).

Thanks for the comment. We have moved the discussion in Figure 4 to the text, please refer to Lines 284-288 of the revised manuscript.

Figure 1: Report units on the y-axis.

Figure 1 has been revised as suggested.

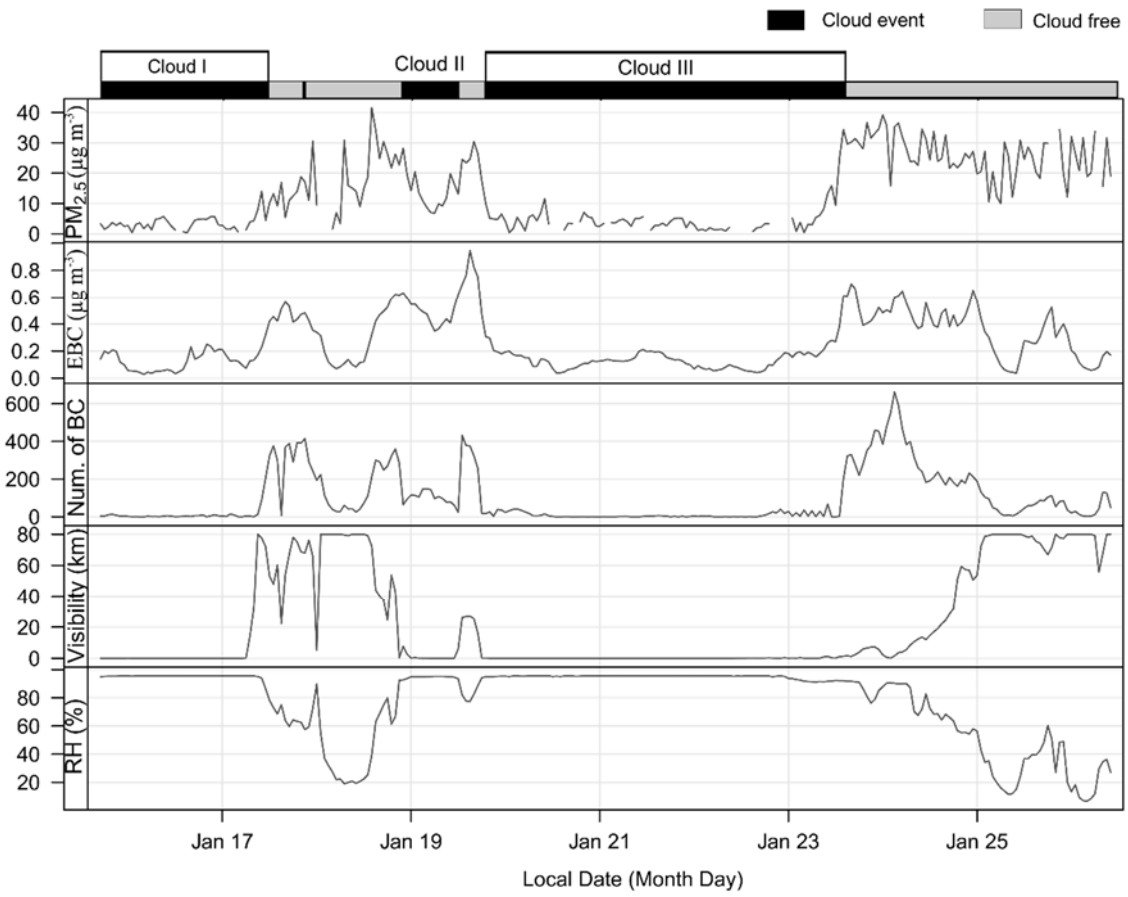

Fig. 1. Temporal profiles (with a 1 hour resolution) of PM2.5, EBC mass concentrations, number of BC-containing particles by SPAMS, RH and visibility. Three cloud events are illustrated with black bars above the figure. $PM_{2.5}$ during the cloud events corresponded to the cloud INT particles. EBC and number of BC-containing particles data were shown for all categories, including the cloud-free, cloud RES, and cloud INT particles. The cloud INT particles were only measured during cloud III.

Figure 4: What were the counts normalized to?

The counts were normalized to the average count over the size range. We have added this information in the caption of the Figure 4.

References

Babu, S. S., Moorthy, K. K., Manchanda, R. K., Sinha, P. R., Satheesh, S. K., Vajja, D. P., … Kumar, V. H. A. (2011). Free tropospheric black carbon aerosol measurements using high altitude balloon: Do BC layers build their own homes up in the atmosphere? Geophysical Research Letters, 38(8). https://doi.org/10.1029/2011GL046654.

Cheng, Y. F., et al. (2006), Mixing state of elemental carbon and non-light-absorbing aerosol components derived from in situ particle optical properties at Xinken in Pearl River Delta of China, J. Geophys. Res., 111, D20204, doi: 10.1029/2005JD006929.

Liu, D., Flynn, M., Gysel, M., Targino, A., Crawford, I., Bower, K., … Coe, H. (2010). Single particle characterization of black carbon aerosols at a tropospheric alpine site in Switzerland. Atmospheric Chemistry and Physics, 10(15), 7389–7407. https://doi.org/10.5194/acp-10-7389-2010

Pósfai, M., Anderson, J. R., Buseck, P. R., & Sievering, H. (1999). Soot and sulfate aerosol particles in the remote marine troposphere. Journal of Geophysical Research: Atmospheres, 104(D17), 21685–21693. https://doi.org/10.1029/1999JD900208

Pusechel, R. F., Blake, D. F., Snetsinger, K. G., Hansen, A. D. A., Verma, S., & Kato, K. (1992). Black carbon (soot) aerosol in the lower stratosphere and upper troposphere. Geophysical Research Letters, 19(16), 1659–1662.

https://doi.org/10.1029/92GL01801

Schwarz, J. P., Samset, B. H., Perring, A. E., Spackman, J. R., Gao, R. S., Stier, P., … Fahey, D. W. (2013). Global-scale seasonally resolved black carbon vertical profiles over the Pacific. Geophysical Research Letters, 40(20), 5542–5547. https://doi.org/10.1002/2013GL057775

Wang, Q., Huang, R.-J., Cao, J., Han, Y., Wang, G., Li, G., Wang, Y., Dai, W., Zhang, R., and Zhou, Y. (2014). Mixing State of Black Carbon Aerosol in a Heavily Polluted Urban Area of China: Implications for Light Absorption Enhancement. Aerosol Sci. Technol., 48(7):689–697. http://doi.org/10.1080/02786826.2014.917758

Reference

Hammer, E., Gysel, M., Roberts, G. C., Elias, T., Hofer, J., Hoyle, C. R., Bukowiecki, N., Dupont, J. C., Burnet, F., Baltensperger, U., and Weingartner, E.: Size-dependent particle activation properties in fog during the ParisFog 2012/13 field campaign, Atmos. Chem. Phys., 14, 10517-10533, doi:10.5194/acp-14-10517-2014, 2014.

Henning, S., Weingartner, E., Schmidt, S., Wendisch, M., Gaggeler, H. W., and Baltensperger, U.: Size-dependent aerosol activation at the high-alpine site Jungfraujoch (3580 m asl), Tellus B, 54, 82-95, 2002.

Matsui, H.: Black carbon simulations using a size- and mixing-state-resolved three-dimensional model: 2. Aging timescale and its impact over East Asia, J. Geophys. Res.-Atmos., 121, 1808-1821, doi:10.1002/2015jd023999, 2016.

Schroder, J. C., Hanna, S. J., Modini, R. L., Corrigan, A. L., Kreidenwies, S. M., Macdonald, A. M., Noone, K. J., Russell, L. M., Leaitch, W. R., and Bertram, A. K.: Size-resolved observations of refractory black carbon particles in cloud droplets at a marine boundary layer site, Atmos. Chem. Phys., 15, 1367-1383, doi:10.5194/acp-15-1367-2015, 2015.

Shingler, T., Dey, S., Sorooshian, A., Brechtel, F. J., Wang, Z., Metcalf, A., Coggon, M., Mulmenstadt, J., Russell, L. M., Jonsson, H. H., and Seinfeld, J. H.: Characterisation and airborne deployment of a new counterflow virtual impactor inlet, Atmos. Meas. Tech., 5, 1259-1269, doi:10.5194/amt-5-1259-2012, 2012.

Zaveri, R. A., Barnard, J. C., Easter, R. C., Riemer, N., and West, M.: Particle-resolved simulation of aerosol size, composition, mixing state, and the associated optical and cloud condensation nuclei activation properties in an evolving urban plume, J. Geophys. Res.-Atmos., 115, 1383-1392, doi:10.1029/2009jd013616, 2010.

Zhang, G., Lin, Q., Peng, L., Yang, Y., Fu, Y., Bi, X., Li, M., Chen, D., Chen, J., Cai, Z., Wang, X., Peng, P., Sheng, G., and Zhou, Z.: Insight into the in-cloud formation of oxalate based on in situ measurement by single particle mass spectrometry, Atmos. Chem. Phys. Discuss., 2017, 1-39, doi:10.5194/acp-2017-763,

2017.

Zuberi, B., Johnson, K. S., Aleks, G. K., Molina, L. T., and Laskin, A.: Hydrophilic properties of aged soot, Geophys. Res. Lett., 32, 67-106, doi:10.1029/2004gl021496, 2005.