Interactive comment on "External and Internal CCN Mixtures: Controlled Laboratory Studies of Varying Mixing States" by Diep Vu et al.

Anonymous Referee #3

The manuscript represents a method of CCN data analysis for different mixtures of organic and inorganic components of varying mixing states with regards to the observed activation and hygroscopicity. By conducting controlled laboratory experiments of mixing, them transition from external to internal mixtures are effectively mimicked. For mixtures of known hygroscopicity CCN behavior agrees well with traditional Köhler theory. Finally, aerosol water is shown to play a significant role in promoting mixing and can be used to modify mixing states.
The paper is well written and easy to follow, though there are some issues and more thorough discussion should be made in specific sections. A very interesting point of the study is the deconvolution of the activation curves to different sigmoidal curves consistent with those of the different components, as well as the study of the impact of mixing fresh combustion emissions with inorganic and organic aerosols.

Specific comments:
1) More thorough discussion should be made in the study of mixing fresh combustion aerosol with inorganic and organic aerosols. Why is combustion aerosol considered and referred to solely as Black Carbon? Also, the activation curve presented in Fig.07 does not reach an obvious plateau, how can we speak about a "homogeneous mixture of black and brown carbon"? Also I would expect that as a homogenous mixture, the activation curve would be a lot steeper, especially in the larger particle size range. Can you please clarify/comment on this?

→ The combustion aerosol generated by the APG is used as a black carbon surrogate; it was not fully speciated in this study. The miniCAST utilized in the APG has been well characterized in previous work (e.g., Pinho et al. 2008; Seong and Boehman 2012; Mamakos et al. 2013; Maricq and Matti Maricq 2014; Durdina et al. 2016; Moore et al. 2014) . The combustion aerosol does contains black and oxidized carbon. Since there are no plateaus in the CCN activation of the soot, (it is a single smooth curve) this suggests that the size-resolved chemical composition is a homogenous (internal) mixture. The slope is indicative of activation at higher mobility diameters where it is known that the transfer function of the DMA is wider, thus contributing to a shallow slope (e.g., Lance et al., 2013).
→ We have revised the text with this added information.

2) A more thorough review of the current literature should be made, as there are relevant studies that are not mentioned. E.g. L69-70 Moore et al., 2012 provide an in-depth analysis of ambient CCN measurements during the 2010 Deepwater Horizon Oil Spill, both studying hygroscopicity vs mixing state and type of size distributions and droplet activation kinetics.

→ We have added the suggested references.

→ Moore et al, 2012 is one of many papers that studies changes of ambient CCN with mixing state. We have included the reference. An extensive literature review will show that there are many papers discuss aerosol mixing state and cloud condensation nuclei. We have added them in this revision. However, The majority of theses papers use ambient data sets of unspeciated aerosol composition. To our knowledge, we are the only manuscript to show changes in laboratory CCN with controlled changes in mixing state aerosol population. This is the novelty of the presented technique. Previous papers (dating back to the early 70's) have provided the theory and have shown the activation of laboratory externally mixed aerosol and internally mixed systems, separately. We have yet to find a paper that has controlled and measured the change from external to internal in the laboratory. We regret that this uniqueness did not come across in the first revision of the paper and thus we have spent considerable effort emphasizing the importance of the new technique presented in the revised manuscript.

→ The following text has been revised as follows.

Knowledge of the mixing state and the chemical composition can greatly improve CCN predictions and has been the focus of several studies (e.g., but not limited to (Bilde and Svenningsson 2004; Abbatt et al. 2005; Henning et al. 2005; Svenningsson et al. 2006; King et al. 2007; Cubison et al. 2008; Kuwata and Kondo 2008; Zaveri et al. 2010; Su et al. 2010; Wang et al. 2010; Spracklen et al. 2011; Ervens et al. 2010; Asa-Awuku et al. 2011; Liu et al. 2013; Jurányi et al. 2013; Paramonov et al. 2013; Padró et al. 2012; Moore et al. 2012; Meng et al. 2014; Bhattu and Tripathi 2015; Almeida et al. 2014; Schill et al. 2015; Crosbie et al. 2015; Che et al. 2016; Ching et al. 2016; Mallet et al. 2017; Sánchez Gácita et al. 2017; Cai et al. 2018; Schmale et al. 2018; Mahish et al. 2018; Kim et al. 2018; Chen et al. 2019; Stevens and Dastoor 2019)

3) CCN activity also depends on the atmospheric processing as well. L50-51 it is stated that CCN activity is complicated when inorganic salts are internally mixed with a complex organic. It has been shown in filed studies that even within a few hours of processing, hygroscopicity (thus activity as well) becomes more or less constant, e.g. Lathem et al., 2013; Bougiatioti et al., 2009. This, to my opinion, should be mentioned.

→ We agree CCN activity and the mixing state of the population depends on atmospheric processing. We have included this in the text. We have added the suggested additional references. Again, our challenge here is that there are a lot of global ambient CCN activity measurements that show changing CCN behaviour. The models to describe changes in CCN mixtures have been validated with ambient measurements. To our knowledge, we are the first to validate with known composition and control subsequent CCN from external to internal mixtures in the laboratory.

Technical corrections:

L109 What type of SMPS, sizing range and of CCNc? It is mentioned in Section 2.3. but it seems to me as missing information to me at that early stage.

→ The instrument specifics were organized into a single section under 'measurement and instrumentation'. The text has been updated with text directing the reader to refer to section 2.3 for instrument specifications

L293 What do the authors mean by "does not account for non-spherical fractal particles"?

→ The apparent hygroscopicity is calculated from the electrical mobility diameter that assumes particles are spherical. Electrical mobility diameter measurement does not take into account non-spherical fractal particles. We have elaborated this in revised text.

Fig.05 Some points exhibit huge variation

→ The variation can be attributed to the conversion from AMS mass to number.

→ References.

1. Abbatt, J. P. D., Broekhuizen, K. and Pradeep Kumar, P.: Cloud condensation nucleus activity of internally mixed ammonium sulfate/organic acid aerosol particles, Atmos. Environ., 39(26), 4767–4778, 2005.
2. Asa-Awuku, A., Moore, R. H., Nenes, A., Bahreini, R., Holloway, J. S., Brock, C. A., Middlebrook, A. M., Ryerson, T. B., Jimenez, J. L., DeCarlo, P. F., Hecobian, A., Weber, R. J., Stickel, R., Tanner, D. J. and Huey, L. G.: Airborne cloud condensation nuclei measurements during the 2006 Texas Air Quality Study, J. Geophys. Res., 116(D11), doi:10.1029/2010JD014874, 2011.
3. Bhattu, D. and Tripathi, S. N.: CCN closure study: Effects of aerosol chemical composition and mixing state, J. Geophys. Res. D: Atmos., 120(2), 766–783, 2015.
4. Bilde, M. and Svenningsson, B.: CCN activation of slightly soluble organics: the importance of small amounts of inorganic salt and particle phase, Tellus B Chem. Phys. Meteorol., 56(2), 128–134, 2004.
5. Bond, T. C., Doherty, S. J., Fahey, D. W., Forster, P. M., Berntsen, T., DeAngelo, B. J., Flanner, M. G., Ghan, S., Kärcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P. K., Sarofim, M. C., Schultz, M. G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S. K., Hopke, P. K., Jacobson, M. Z., Kaiser, J. W., Klimont, Z., Lohmann, U., Schwarz, J. P., Shindell, D., Storelvmo, T., Warren, S. G. and Zender, C. S.: Bounding the role of black carbon in the climate system: A scientific assessment, J. Geophys. Res. D: Atmos., 118(11), 5380–5552, 2013.
6. Cai, M., Tan, H., Chan, C. K., Qin, Y., Xu, H., Li, F., Schurman, M. I., Liu, L. and Zhao, J.: The size-resolved cloud condensation nuclei (CCN) activity and its prediction based on aerosol hygroscopicity and composition in the Pearl Delta River (PRD) region during wintertime 2014, Atmos. Chem. Phys., 18(22), 16419–16437, 2018.
7. Chen, L., Li, Q., Wu, D., Sun, H., Wei, Y., Ding, X., Chen, H., Cheng, T. and Chen, J.: Size distribution and chemical composition of primary particles emitted during open biomass burning processes: Impacts on cloud condensation nuclei activation, Sci. Total Environ., 674, 179–188, 2019.
8. Ching, J., Riemer, N. and West, M.: Black carbon mixing state impacts on cloud microphysical properties: Effects of aerosol plume and environmental conditions, JOURNAL OF GEOPHYSICAL RESEARCH-ATMOSPHERES, 121(10), 5990–6013, 2016.
9. Crosbie, E., Youn, J.-S., Balch, B., Wonaschütz, A., Shingler, T., Wang, Z., Conant, W. C., Betterton, E. A. and Sorooshian, A.: On the competition among aerosol number, size and composition in predicting CCN variability: a multi-annual field study in an urbanized desert, Atmos. Chem. Phys., 15, 6943–6958, 2015.
10. Cubison, M. J., Ervens, B., Feingold, G., Docherty, K. S., Ulbrich, I. M., Shields, L., Prather, K., Hering, S. and Jimenez, J. L.: The influence of chemical composition and mixing state of Los Angeles urban aerosol on CCN number and cloud properties, Atmos. Chem. Phys., 8(18), 5649–5667, 2008.
11. Durdina, L., Lobo, P., Trueblood, M. B., Black, E. A., Achterberg, S., Hagen, D. E., Brem, B. T. and Wang, J.: Response of real-time black carbon mass instruments to mini-CAST soot, Aerosol Science and Technology, 50(9), 906–918, doi:10.1080/02786826.2016.1204423, 2016.
12. Dusek, U., Reischl, G. P. and Hitzenberger, R.: CCN activation of pure and coated carbon black particles, Environ. Sci. Technol., 40(4), 1223–1230, 2006.
13. Ervens, B., Cubison, M. J., Andrews, E., Feingold, G., Ogren, J. A., Jimenez, J. L., Quinn, P. K., Bates, T. S., Wang, J., Zhang, Q., Coe, H., Flynn, M. and Allan, J. D.: CCN predictions using simplified assumptions of organic aerosol composition and mixing state: a synthesis from six different locations, Atmos. Chem. Phys., 10(10), 4795–4807, 2010.
14. Henning, S., Rosenørn, T., D'Anna, B., Gola, A. A., Svenningsson, B. and Bilde, M.: Cloud droplet activation and surface tension of mixtures of slightly soluble organics and inorganic salt, Atmos. Chem.

Phys., 5(2), 575–582, 2005.
15. Jurányi, Z., Tritscher, T., Gysel, M., Laborde, M., Gomes, L., Roberts, G., Baltensperger, U. and Weingartner, E.: Hygroscopic mixing state of urban aerosol derived from size-resolved cloud condensation nuclei measurements during the MEGAPOLI campaign in Paris, Atmos. Chem. Phys., 13(13), 6431–6446, 2013.
16. Kim, N., Park, M., Yum, S. S., Park, J. S., Shin, H. J. and Ahn, J. Y.: Impact of urban aerosol properties on cloud condensation nuclei (CCN) activity during the KORUS-AQ field campaign, Atmos. Environ., 185, 221–236, 2018.
17. King, S. M., Rosenoern, T., Shilling, J. E., Chen, Q. and Martin, S. T.: Cloud condensation nucleus activity of secondary organic aerosol particles mixed with sulfate, Geophys. Res. Lett., 34(24), 3589, 2007.
18. Koehler, K. A., DeMott, P. J., Kreidenweis, S. M., Popovicheva, O. B., Petters, M. D., Carrico, C. M., Kireeva, E. D., Khokhlova, T. D. and Shonija, N. K.: Cloud condensation nuclei and ice nucleation activity of hydrophobic and hydrophilic soot particles, Phys. Chem. Chem. Phys., 11(36), 7906–7920, 2009.
19. Kuwata, M. and Kondo, Y.: Dependence of size-resolved CCN spectra on the mixing state of nonvolatile cores observed in Tokyo, Journal of Geophysical Research, 113(D19), doi:10.1029/2007jd009761, 2008.
20. Lammel, G. and Novakov, T.: WATER NUCLEATION PROPERTIES OF CARBON-BLACK AND DIESEL SOOT PARTICLES, Atmos. Environ., 29(7), 813–823, 1995.
21. Liu, D., Allan, J., Whitehead, J., Young, D., Flynn, M., Coe, H., McFiggans, G., Fleming, Z. L. and Bandy, B.: Ambient black carbon particle hygroscopic properties controlled by mixing state and composition, Atmos. Chem. Phys., 13(4), 2015–2029, 2013.
22. Mahish, M., Jefferson, A. and Collins, D. R.: Influence of Common Assumptions Regarding Aerosol Composition and Mixing State on Predicted CCN Concentration, Atmosphere , 9(2), 54, 2018.
23. Mallet, M. D., Cravigan, L. T., Milic, A., Alroe, J., Ristovski, Z. D., Ward, J., Keywood, M., Williams, L. R., Selleck, P. and Miljevic, B.: Composition, size and cloud condensation nuclei activity of biomass burning aerosol from northern Australian savannah fires, Atmos. Chem. Phys., 17(5), 3605–3617, 2017.
24. Mamakos, A., Khalek, I., Giannelli, R. and Spears, M.: Characterization of Combustion Aerosol Produced by a Mini-CAST and Treated in a Catalytic Stripper, Aerosol Science and Technology, 47(8), 927–936, doi:10.1080/02786826.2013.802762, 2013.
25. Maricq, M. M. and Matti Maricq, M.: Examining the Relationship Between Black Carbon and Soot in Flames and Engine Exhaust, Aerosol Science and Technology, 48(6), 620–629, doi:10.1080/02786826.2014.904961, 2014.
26. McMeeking, G. R., Good, N., Petters, M. D., McFiggans, G. and Coe, H.: Influences on the fraction of hydrophobic and hydrophilic black carbon in the atmosphere, Atmos. Chem. Phys., 11(10), 5099–5112, 2011.
27. Meng, J. W., Yeung, M. C., Li, Y. J., Lee, B. Y. L. and Chan, C. K.: Size-resolved cloud condensation nuclei (CCN) activity and closure analysis at the HKUST Supersite in Hong Kong, Atmos. Chem. Phys., 14(18), 10267–10282, 2014.
28. Moore, R. H., Ziemba, L. D., Dutcher, D., Beyersdorf, A. J., Chan, K., Crumeyrolle, S., Raymond, T. M., Thornhill, K. L., Winstead, E. L. and Anderson, B. E.: Mapping the Operation of the Miniature Combustion Aerosol Standard (Mini-CAST) Soot Generator, Aerosol Science and Technology, 48(5), 467–479, doi:10.1080/02786826.2014.890694, 2014.
29. Padró, L. T., Moore, R. H., Zhang, X., Rastogi, N., Weber, R. J. and Nenes, A.: Mixing state and compositional effects on CCN activity and droplet growth kinetics of size-resolved CCN in an urban environment, Atmos. Chem. Phys., 12(21), 10239–10255, 2012.
30. Paramonov, M., Aalto, P. P., Asmi, A., Prisle, N., Kerminen, V.-M., Kulmala, M. and Petäjä, T.: The analysis of size-segregated cloud condensation nuclei counter (CCNC) data and its implications for cloud droplet activation, Atmos. Chem. Phys., 13(20), 10285–10301, 2013.
31. Pinho, C. E. L., João M P, Ferreira, V., Pilão, R. and Pinho, C.: Influence of Burner Geometry on Flame Characteristics of Propane-Air Mixture: Experimental and Numerical Studies, Defect and Diffusion Forum, 273-276, 162–167, doi:10.4028/www.scientific.net/ddf.273-276.162, 2008.
32. Riemer, N., Ault, A. P., West, M., Craig, R. L. and Curtis, J. H.: Aerosol Mixing State: Measurements, Modeling, and Impacts, Reviews of Geophysics, doi:10.1029/2018rg000615, 2019.
33. Rojas, L., Peraza, A. and Ruette, F.: Aging Oxidation Reactions on Atmospheric Black Carbon by OH Radicals. A Theoretical Modeling Study, J. Phys. Chem. A, 119(52), 13038–13047, 2015.

34. Sánchez Gácita, M., Longo, K. M., Freire, J. L. M., Freitas, S. R. and Martin, S. T.: Impact of mixing state and hygroscopicity on CCN activity of biomass burning aerosol in Amazonia, Atmos. Chem. Phys., 17(3), 2373–2392, 2017.
35. Schill, S. R., Collins, D. B., Lee, C., Morris, H. S., Novak, G. A., Prather, K. A., Quinn, P. K., Sultana, C. M., Tivanski, A. V., Zimmermann, K., Cappa, C. D. and Bertram, T. H.: The Impact of Aerosol Particle Mixing State on the Hygroscopicity of Sea Spray Aerosol, ACS Cent Sci, 1(3), 132–141, 2015.
36. Seong, H. J. and Boehman, A. L.: Studies of soot oxidative reactivity using a diffusion flame burner, Combustion and Flame, 159(5), 1864–1875, doi:10.1016/j.combustflame.2012.01.009, 2012.
37. Spracklen, D. V., Carslaw, K. S., Poschl, U., Rap, A. and Forster, P. M.: Global cloud condensation nuclei influenced by carbonaceous combustion aerosol, Atmos. Chem. Phys., 11(17), 9067–9087, 2011.
38. Stevens, R. and Dastoor, A.: A Review of the Representation of Aerosol Mixing State in Atmospheric Models, Atmosphere , 10(4), 168, 2019.
39. Su, H., Rose, D., Cheng, Y. F., Gunthe, S. S., Massling, A., Stock, M., Wiedensohler, A., Andreae, M. O. and Pöschl, U.: Hygroscopicity distribution concept for measurement data analysis and modeling of aerosol particle mixing state with regard to hygroscopic growth and CCN activation, Atmospheric Chemistry and Physics, 10(15), 7489–7503, doi:10.5194/acp-10-7489-2010, 2010.
40. Svenningsson, B., Rissler, J., Swietlicki, E., Mircea, M., Bilde, M., Facchini, M. C., Decesari, S., Fuzzi, S., Zhou, J., Mønster, J. and Rosenørn, T.: Hygroscopic growth and critical supersaturations for mixed aerosol particles of inorganic and organic compounds of atmospheric relevance, Atmos. Chem. Phys., 6(7), 1937–1952, 2006.
41. Wang, J., Cubison, M. J., Aiken, A. C., Jimenez, J. L. and Collins, D. R.: The importance of aerosol mixing state and size-resolved composition on CCN concentration and the variation of the importance with atmospheric aging of aerosols, Atmos. Chem. Phys., 10(15), 7267–7283, 2010.
42. Weingartner, E., Burtscher, H. and Baltensperger, U.: Hygroscopic properties of carbon and diesel soot particles, Atmospheric Environment, 31(15), 2311–2327, doi:10.1016/s1352-2310(97)00023-x, 1997.
43. Winkler, P.: The growth of atmospheric aerosol particles as a function of the relative humidity—II. An improved concept of mixed nuclei, J. Aerosol Sci., 4(5), 373–387, 1973.
44. 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. D: Atmos., 115(D17) [online] Available from: https://onlinelibrary.wiley.com/doi/pdf/10.1029/2009JD013616, 2010.