Manuscript No.: acp-2020-625

Title: Large contribution of organics to condensational growth and formation of cloud condensation nuclei (CCN) in remote marine boundary layer

We thank the anonymous referees for their valuable and constructive comments/suggestions on our manuscript. We have revised the manuscript accordingly and please find our point-to-point responses below.

Comments by Anonymous Referee #2:

General Comments:

Through size-resolved CCN and HTDMA measurements the authors present evidence for a substantial role of organics in the condensational growth of particles to CCN sizes in the remote marine boundary layer. There is no shortage of aerosol organics in the marine atmosphere but there is a lack of information about their sources and impacts.This paper provides information about the role they may play in CCN formation. The paper should be published after the concerns listed below have been addressed.

Detailed Comments:

1. Line 34: "It has long been recognized: : :" adding a few references going further back than 2018 would be appropriate.

Responses:

Following the reviewer's suggestion, we've added more references, and the sentence now reads:

"It has long been recognized that sulfate produced from DMS oxidation is a major species for particle condensational growth in the remote marine environment (Charlson et al., 1987; O'Dowd et al., 1999; Pandis et al., 1994; Raes and Van Dingenen, 1992; Sanchez et al., 2018)."

2. Lines 112 – 113: What is the uncertainty associated with the SO2 and MSA concentrations derived from MERRA-2?

Responses:

As far as we know, currently there's no uncertainty study or comparison with observations for MERRA-2 SO_2 and MSA concentrations over the open oceans of Eastern North Atlantic. Over the East Asia where SO_2 is mainly from anthropogenic emissions, monthly averaged surface SO_2 concentrations from MERRA-

2 were compared to measurements at 46 sites of The Acid Deposition Monitoring Network in East Asia (EANET) during the period from 2001 to 2008 (Randles et al., 2016). The relative biases (the ratio of MERRA-2 to EANET) range from 0.968 in winter to 1.418 in the fall, with correlation varying between 0.319 to 0.501 (Randles et al., 2016).

Whereas some uncertainties are expected, MERRA-2 likely provides the best estimate of SO_2 and DMS concentration in the absence of measurements. We also note that the conclusions of this study are not based on the absolute concentrations. Rather, we use the relative trends of SO_2 and DMS concentrations to infer the potential sources, which is expected to be less influenced by the uncertainties in the concentrations.

3. Lines 201 – 202 and Figure S1 caption: These seem contradictory. The main text says "The difference is close to the measurements uncertainty…. therefore the major condensing species is classified as (NH4)2SO4. The figure caption says "the major condensing species included both organics and sulfates or dominated by (NH4)2SO4".

Responses:

Sorry for the confusion. We've clarified the caption of Fig. S1:

"Figure S1. An example case of deriving $\kappa_{c,CCN}$ and $\kappa_{c,GF}$ for the same growth event. **…** (b) A $\kappa_{c,CCN}$ value of 0.59 (i.e., the sum of slope and intercept) is derived from the linear fitting of κ_{CCN} vs. $f_{V,\,cond}$. This value falls in the intermediate-$\kappa_{c,CCN}$ category~~ and suggests that the major condensing species included both organics and sulfates or dominated by $(NH_4)_2SO_4$~~. (c) A $\kappa_{c,GF}$ value of 0.45 is derived from the variation of κ_{GF} following the same approach. Major condensing species of this case is determined to be $(NH_4)_2SO_4$ (see detailed discussions in section 5 of the main text)."

4. Figure 5 caption: Please describe what the black dashed line in the figure represents.

Responses:

Following the reviewer's suggestion, we've added the description and the caption now reads:

"**Figure 5. Comparison of $\kappa_{c,CCN}$ and $\kappa_{c,GF}$ values for the intermediate $\kappa_{c,CCN}$ category, colored by the measured molar ratios of NH_4^+/SO_4^{2-}.** The black dash line is the 1:1 line, while the cyan dash lines represent the ± 20% uncertainties."

5. Figure 5: There is no clear relationship between the degree of difference between kappa_c,GF and kappa_c,CCN and the NH4 to SO4 molar ratio. If I'm interpreting the figure correctly, there are instances (dark blue points) when the NH4 to SO4 molar ratio is very low but the difference between the kappa values is small. Based on these data, it's not clear that low amounts of NH4 relative to SO4 is most prevalent during intermediate kappa_c,CCN events. Maybe it would be clearer if Figure 5 were expanded to include all data, not just intermediate events.

Responses:

We've clarified this point in the modified manuscript as:

"In addition, chemical composition of sub-micron non-refractory aerosol ($NR\text{-}PM_1$; aerodynamic diameters below 1 μm) indicates an ammonium-poor condition over the ENA (color bar in Fig. 5), typical of remote marine environment (Adams et al., 1999). Therefore, sulfate is not fully neutralized as $(NH_4)_2SO_4$. Note that the bulk NH_4^+/SO_4^{2-} molar ratio shown in Fig. 5 is dominated by that of accumulation mode particles, whereas the $\kappa_{c,CCN}$ and $\kappa_{c,GF}$ values are derived from growing Aitken mode particles. Whereas the degrees of neutralization for accumulation and Aitken modes are expected to correlate with each other (e.g., lower neutralization degrees for both accumulation and Aitken modes under more ammonium poor conditions), it is possible that the neutralization degree may exhibit size dependence under some circumstances. For example, in-cloud formation of SO_4^{2-} influences the neutralization degree of accumulation mode particles only (Seinfeld and Pandis, 2016), possibly leading to a lower degree of neutralization for accumulation mode. This could explain a few data points that exhibit lower degree of neutralization but similar $\kappa_{c,CCN}$ and $\kappa_{c,GF}$ values."

6. Lines 231 – 232: It is stated that kappa_c,CCN is not correlated with the NR-PM1 organic/sulfate ratio suggesting different sources of the condensed species in pre-CCN and the accumulation mode particle composition. Does this lack of a correlation suggest anything about the importance of the pre-CCN condensed species in terms of CCN activity or concentration since the accumulation mode can dominate the CCN concentration?

Responses:

We agree that accumulation mode can dominate the CCN concentration. On the other hand, condensational growth of the pre-CCN represents a major source of CCN in marine boundary layer (Sanchez et al., 2018; Zheng et al., 2018), and this is the focus of this study. In MBL, once pre-CCN particles grow to sufficient size (e.g., Hoppel minimum diameter) and become CCN, their composition continuously evolves, for example, through in cloud production of sulfate and organics. Therefore, it is not surprising that $\kappa_{c,CCN}$ is not well correlated with accumulation or bulk particle composition under certain conditions. However, the lack of correlation does not suggest that the condensation growth of pre-CCN is not an important source of CCN in MBL.

References

Adams, P. J., Seinfeld, J. H., and Koch, D. M.: Global concentrations of tropospheric sulfate, nitrate, and ammonium aerosol simulated in a general circulation model, Journal of Geophysical Research: Atmospheres, 104, 13791-13823, 1999.

Charlson, R. J., Lovelock, J. E., Andreae, M. O., and Warren, S. G.: Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate, Nature, 326, 655-661, 1987.

O'Dowd, C. D., Lowe, J. A., and Smith, M. H.: Observations and modelling of aerosol growth in marine stratocumulus—case study, Atmospheric Environment, 33, 3053-3062, 1999.

Pandis, S. N., Russell, L. M., and Seinfeld, J. H.: The relationship between DMS flux and CCN concentration in remote marine regions, Journal of Geophysical Research: Atmospheres, 99, 16945-16957, 1994.

Raes, F. and Van Dingenen, R.: Simulations of condensation and cloud condensation nuclei from biogenic SO2 in the remote marine boundary layer, Journal of Geophysical Research: Atmospheres, 97, 12901-12912, 1992.

Randles, C., da Silva, A., Buchard, V., Darmenov, A., Colarco, P., Aquila, V., Bian, H., Nowottnick, E., Pan, X., and Smirnov, A.: The MERRA-2 aerosol assimilation, NASA Tech. Rep. Series on Global Modeling and Data Assimilation, 45, 2016.

Sanchez, K. J., Chen, C.-L., Russell, L. M., Betha, R., Liu, J., Price, D. J., Massoli, P., Ziemba, L. D., Crosbie, E. C., Moore, R. H., Müller, M., Schiller, S. A., Wisthaler, A., Lee, A. K. Y., Quinn, P. K., Bates, T. S., Porter, J., Bell, T. G., Saltzman, E. S., Vaillancourt, R. D., and Behrenfeld, M. J.: Substantial Seasonal Contribution of Observed Biogenic Sulfate Particles to Cloud Condensation Nuclei, Sci Rep-Uk, 8, 3235, 2018.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to climate change, John Wiley & Sons, 2016.

Zheng, G., Wang, Y., Aiken, A. C., Gallo, F., Jensen, M. P., Kollias, P., Kuang, C., Luke, E., Springston, S., Uin, J., Wood, R., and Wang, J.: Marine boundary layer aerosol in the eastern North Atlantic: seasonal variations and key controlling processes, Atmos. Chem. Phys., 18, 17615-17635, 2018.