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Comment on acp-2022-387

Anonymous Referee #1

Referee comment on "Organic enrichment in droplet residual particles relative to out of cloud over the northwestern Atlantic: analysis of airborne ACTIVATE data" by Hossein Dadashazar et al., Atmos. Chem. Phys. Discuss.,
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This manuscript presents an interesting data set derived from airborne measurement by an AMS during the first 4 ACTIVATE campaigns over the Atlantic Ocean east of Virginia. The AMS sampled aerosol above and below marine boundary layer clouds, in and above the boundary layer in cloud free air; and cloud droplet residual particles sampled through a CVI. The main finding was that the droplet residual particles generally showed large enhancements of the organic mass fraction compared to aerosol sampled out of cloud, both very near to clouds as well as in clear air regions. The organic material in the droplet residuals also tended to be more oxidized than the organic material in aerosol out of cloud.

The authors make a convincing argument that the increased organic fraction in the droplet residuals is more likely the result of aqueous processing in cloud (their hypothesis) (or possibly in the CVI (my tentative alternate suggestion)) than preferential activation of the organic rich aerosol when the clouds formed. They suggest that incorporation, and apparent oxidation, of organic mass in cloud droplets will result in aerosol that is enriched in organics after the droplets evaporate, which could have important implications regarding the subsequent ability of the MBL aerosol population to act as CCN (organic rich aerosol might be less effective CCN than sulfate dominated aerosol). Most models do not include aqueous processes that enrich cloud droplets in organic matter, and tend to predict that sulfate should be the dominant component of the MBL aerosol and constitute the main fraction of the CCN population.

However, there is a critical aspect of the data set that makes it unclear whether the apparent enrichment of oxidized organic matter in droplet residual particles actually has a significant impact on the composition of MBL aerosol. One would expect that aerosol just above or below clouds that have droplets greatly enriched in organics would also show some enhancement compared to aerosol that had not been cloud processed. This was not observed. In fact, Table 1 shows that the average organic mass fraction of aerosol in cloud free BL was higher than observed just below clouds in all four of the bins (non-CAO, CAO,

May-Jun, and Aug-Sep). The same is true when one compares the average organic mass fraction between clear air aerosol above the top of the boundary layer and that sampled just above clouds. Given that clear air sampling was "generally closer to the coast" (line 110) and thus generally upwind of the regions where clouds were sampled, these observations seem to suggest that cloud processing tends to increase sulfate relative to organics in the aerosol, regardless of the very large enhancement of organic mass fraction in the cloud droplet residual particles.

The authors do admit this "problem" nearly in passing (lines 342-344) but do not fully explore or explain it. Here I offer a number of possibilities that should be considered. First, there may be some artifact in the CVI causing the enrichment in oxidized organics measured by the AMS. This does not seem too likely but needs to be investigated and ruled out. Another possibility could be that the cloud drops truly are greatly enriched in organics, but when the droplets evaporate much of this material is also volatile enough to return to the gas phase without producing aerosol highly enriched in organics. Perhaps a large fraction of the organic rich cloud droplets continue to grow large enough to precipitate, again leaving no highly enriched aerosol behind. My final possible explanation may be the most optimistic. Maybe there is evidence of organic-rich cloud-processed aerosol in the data set that is lost in the averages but clear in case studies. For example, might the increase in organic mass fraction ACT in cloud legs 5 and 6 on RF 5 (Fig S7) be a hint of evaporated cloud droplets vented above the clouds (of course it is a little problematic that the organic mass fraction remains high ACT for the rest of the flight). It might be worth looking particularly at BBL and ABL legs downwind of, and soon after, cloud legs to see if there are organic rich cloud processed aerosol there (possibly contributing to the high averages reported in Table 1).

In summary, as noted at the start, this is an interesting data set, but I am not convinced that the suggested implications are supported. The inference that organic rich particles reaching the AMS behind the CVI are reflecting the composition of cloud droplets and will lead to organic rich aerosol needs to be better supported.

A number of editorial comments follow, keyed to line numbers:

62 does higher or lower MBL height and liquid cloud fraction "promote stronger aerosol-cloud interactions"?

68/69 "Or particular" should be "Of particular"

76-79 Not clear to me how knowing the composition of droplet residuals directly tells us about composition of CCN, especially if there is aqueous processing active in the droplets.

108 It seems like the cloud-free ensembles ought to be closer to 15 minutes than 35.

128-131 Rationale for ignoring cloud water composition could be simplified to just note that the partial speciation of organics in the cloud water samples makes it hard to compare to AMS total organics.

132-133 Might be prudent to just say that smearing in the PILS used in ACTIVATE was problematic, and not imply that all PILS suffer extreme smearing. See Zeng et al., 2021 (AMT, 14, 6357-6378, <https://doi.org/10.5194/amt-14-6357-2021> for a description of how modifications greatly reduced smearing in the PILS NOAA flew during FIREX AQ.

136-142 Why were trajectories only calculated for cloud free points (I assume this means BBL and ABL points)? If you actually have trajectories for BCB and ACT legs as well this should be made clear.

215 seems to be missing one or more words. Maybe something like "source aloft that might include..."

217 should "boundary clouds" be "boundary layer clouds"?

229-230 double check Table 1. I only looked closely at Organic and Sulfate but noticed that for ACT Non-CAO the concentrations show $\text{Org} > \text{SO}_4$ but MF has $\text{SO}_4 > \text{Org}$. Same is true for ACT May-Jun and also for ABL CAO.

266-270 related to comment on lines 76-79. If your main conclusion is that aqueous processing is adding a lot of organics to cloud droplets, it is not certain that measuring the composition of droplet residual particles tells us anything definite about the composition of the CCN, which are what the Nd is dependent on.

288-289 Why include nitrate in Fig 5, seems pretty distant from your story?

319-320 Probably should have justified the exclusion of ACT legs in discussion of Fig 5 before this.

327-341 Not compelling evidence that there are no CVI artifacts.

342-348 As noted in my review, this is a big problem that needs much more careful discussion than these few sentences. Seems you are suggesting that the interstitial aerosol (that would not appear in the droplet residuals) may be very enriched in SO₄, masking any organic-rich cloud-processed aerosol coming out of the cloud. But the BBL and ABL samples suggest that aerosol in airmasses upwind of the clouds tends to be organic-rich, especially compared to BCB and ACT.

401-413 Discussion of Fig 9 is interesting, but you have not established that any of the organics in aerosol sampled outside of cloud were added to the aerosol phase through aqueous processing in the cloud.

443-460 Conclusions probably need to be revisited if you cannot establish that the droplet residual composition ever truly contributes significant aerosol with enhanced organics after the clouds dissipate.