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Interactive comment on "CCN activity of six pollenkitts and the influence of their surface activity" *by* Nønne L. Prisle et al.

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We thank both reviewers for their careful revision of our manuscript, keen eyes on detail, and thoughtful comments.

A common point made by both reviewers relate to the atmospheric implications and impact of the work. Our main motivation for the work has been from the point of cloud microphysics, to evaluate the different Köhler frameworks including surface activity effects for a new type of atmospheric organic aerosol (OA) mixture. There is likely a great variety of surface active OA in the atmosphere, but the diversity of systems which have been analyzed for detailed surfactant effects on cloud microphysical processes is still rather narrow in terms of molecular complexity and compound classes studied

(**?**). As we here observe a somewhat different hygroscopicity response to OA surface activity from previous work, supporting recent atmospherically relevant observations, more such investigations seem both warranted and timely.

Pollenkitt is an example of atmospheric complex biogenic primary OA which is a class of OA that to our knowledge has not previously been subject to such analysis. Pollenkitt was especially well-suited, as extraction of the pollenkitt mixture from collected pollen grains allowed us to obtain sufficient amounts of sample to perform both the cloud condensation nuclei (CCN) and surface tension analysis in parallel, a common challenge for the type of studies in question and a key factor governing the scarcity of studies made for atmospheric OA so far. Furthermore, pollenkitt was interesting due to its unresolved chemical composition and higher aqueous solubility compared to most previously studied systems. It is possible that pollenkitt has similarities to other water soluble surface active biogenic OA, but that remains to be further established. Mixing with ammonium sulfate salt in the aqueous phase has atmospheric relevance considering aging processes in various environments, including polluted air masses and cloud processing, but is also used here as a physico-chemical indicator of surface activity effects, highlighting the magnitude of characteristic signatures of OA aqueous surface activity.

The context and intended impact of this work therefore lies primarily in challenging and widening our understanding of atmospheric surface active OA and specifically how surface activity impacts cloud microphysics, which remains one of the key parameters introducing uncertainties in predicted CCN and cloud droplet number concentrations in the atmosphere (**???**, and references therein). Specifically for pollen, our present results contribute to laying out the foundation for a more general and comprehensive treatment of atmospheric effects by enabling modeling of hygroscopic water uptake and cloud formation across a wide range of conditions, e.g. humidity regimes and particle size distributions, accounting for individual sizes and shapes of pollen grains and fragments, fractions of pollenkitt and possible presence of inorganic secondary aerosol. Pollen comes in a great variety of shapes and sizes (?, e.g.). A decoupled understanding of contributions from different pollen components is therefore essential for modeling water interactions across a wide range of atmospheric conditions, which may not all be feasible to reproduce in controlled experiments.

Such a treatment will require further model development and is the focus of ongoing efforts in collaboration with the regional and global modeling community. In addition to providing information and enabling modeling of the cloud forming potential of pollen grains and fragments, CCN activity analysis is also simply a means to characterize water interactions of small amounts of sample material. Such interactions are critical to the role of pollenkitt in transportation and biological functions of pollen, but a detailed study of the impact of our results on these processes lies outside the scope of this work.

We have modified the abstract, introduction and conclusions sections of our manuscript to clarify these points, and added an example (Section 4) illustrating how the specific pollenkitt hygroscopicity determined in this work can be used for predictions of overall CCN activity for pollen grains of different sizes, with and without the presence of ammonium sulfate.

Below we respond to specific comments from **Referee #1** in a point-wise fashion.

Specific comments:

1. Dp,50 often referred to as a critical diameter throughout the study should be referred to as the dry activation diameter or similar. It is easy to confuse this with the critical point of the köhler curve, and the change will make terminology consistent with Moore et al. 2010.

   We now refer to $D_{p,50}$ as critical dry diameter throughout the manuscript, following the terminology of e.g. ? and ?.

2. It would be useful to see Figure 2 plotted against particle size, along with the köhler curves as predicted by the four models.

   Figure 2 shows measurements of bulk solution surface tension made from pendant drops that were not varied in size, so it is not possible to plot Fig. 2 against particle size along with the Köhler curves. The pendant drops are large enough to be considered purely macroscopic (bulk) solutions and therefore (unfortunately!) do not contain any information of size dependent surface tension. In case the reviewer refers to the evolution of modeled concentration dependent surface tension with dilution of a droplet and the impact on the shape of the Köhler curve, this has been shown in several previous studies, e.g. ?, ?, ?, ?, and ?, and for the sake of brevity we therefore focus here on the variation of predicted droplet surface tension at activation across different dry particle sizes and compositions.

3. Page 2, line 28: Is the data available to quantify these high humidities? Or at least specify sub- or supersaturated?

   Yes, the humidities are available. The text has been updated with references to the experiments and now reads:

   “Steiner et al. (2015) characterized the cloud droplet forming potential (CCN activity) of so-called submicron subpollen particles (SSP), which form as fragments from whole pollen grains. Laboratory experiments found whole pollen grains can rupture and release SSP when wetted by direct contact with liquid water or exposure to high ambient relative humidities of 80–96% (????).”

4. Page 3, line 32: Ovadnevaite et al study better characterised as a coastal rather than oceanic location. Furthermore, the aerosol size distribution and chemical composition they studied is not representative of marine aerosol at large – I suggest removing “with potential global implications due to the relative significance of marine aerosol”. See Heintzenberg et al (2000), for example, for comparison.

   We have clarified the location and environment studied by ? but kept “with potential global implications due to the relative significance of marine aerosol.” ?

include data from Mace Head in their overview of marine aerosols, and **?** specifically study North Atlantic marine air masses.

"Ovadnevaite et al. (2017) soon after showed that there may be evidence for such mechanisms in observations of primary organic aerosol (POA) from a coastal environment at Mace Head, with potential global implications due to the relative significance of marine aerosol."

5. Page 3, line 6: Around here I suggest adding the reference Lowe et al. (2016) – uses 4 surfactant models, very similar conceptually to those in this study, to model CCN spectra across a similar range of supersaturations.

   The reference has been added, in the suggested and a couple of additional places. We thank the reviewer for the suggestion.

   ". . . and model-generated synthetic aerosol representing a variety of atmospheric environments (**?**), demonstrated how surface activity and its effect on cloud condensation nuclei (CCN) activity involve complex non-linear interactions between both surface tension and bulk-to-surface partitioning in droplets."

6. Page 4, line 32: State that this is Dp,50

   Done.

7. Page 4, line 34: State somewhere the numerical values of all supersaturation bands.

   Done.

   "The CCN counter was operated at nine different supersaturations (0.10, 0.21, 0.38, 0.51, 0.69, 0.90, 1.0, 1.3, and 1.4%) for 20 minutes each so that approximately eight complete size distributions from the DMA are sampled at each supersaturation."

8. Page 5, line 7: Is there some rationale for choosing this mass fraction? I guess to be a representative aerosol composition in a vegetation-rich region. I think it would be beneficial to add some motivating text. Furthermore, it would be have been nice to see how the results and conclusions might change subject to a varying mass fraction. I recommend including something to this effect in the revisions if possible.

   We have added the following section to clarify the choice of organic–inorganic mixing ratio:

   "Mixing with ammonium sulfate salt in the aqueous phase is a simple way to mimic atmospheric aging in various environments, such as cloud processing and formation of secondary inorganic aerosol in polluted air, but is also used here as a physico-chemical indicator to highlight the presence and magnitude of characteristic signatures of aqueous surface activity (**??**). The specific organic–inorganic mass mixing ratio was chosen based on observations from previous work that (*i*) surface activity effects became evident in cloud droplet activation behavior of particles with more than about 50% by mass of surface active organic aerosol (**??**), (*ii*) additional effects of organic–inorganic solute interactions were predicted to be most prominent for mass mixing ratios in the range of 80-95% surface active organic mass (**??**), and (*iii*) among these particle compositions, the lower ratios of surface active organic are likely to be the more atmospherically relevant in general (**??**). However, as pollenkitt is a pollen grain borne POA, the actual range of organic–inorganic mixing ratios resulting from atmospheric processing remain speculative."

   In the present work we have focused on surface activity effects as they vary across particle size, rather than organic–inorganic composition. One of the main reasons for this is the relative scarcity of pollenkitt sample. In order to sufficiently constrain mixing ratio variations, we would need to measure surface tensions and CCN activity across a wide range of compositions and a new sample stock solution would have been needed in each case. On the contrary, sample concentration in case of surface tension measurements and dry particle size in case of CCN activity measurements can be varied from a single stock solution. We have added the following sentence to clarify this limitation:

"A full characterization of mixing effects with the methods applied here would require preparation of fresh stock solutions for each organic–inorganic composition. Due to the relative scarcity of pollenkitt samples, measurements were therefore limited to one AS mixing ratio for each of the two pollenkitt mixtures."

9. Page 7, line 19: Is c_PK the total concentration for the bulk model and surface phase concentration in the partitioning model? If so, would be good to clarify here.

   The concentration dependent surface tension is specifically parametrized as a function of solution bulk concentration, which for macroscopic (bulk) solutions for all purposes is identical to the total concentration. In sub-micron droplets, surface partitioning depletes the bulk and we correct for this when using the parametrization based on bulk concentrations to evaluate droplet surface tension. We have now tried to emphasize this in the appropriate places throughout the text, in particular Section 2.4.

10. Page 8, section 2.5: state what you are assuming for surface tension for this procedure. If sigma=sigma_w then change in Eq. 1. Otherwise the reader doesn't get this information until page 12 line 19.

    In Eq. (1), we have expressed Köhler Theory in its canonical form without any assumptions. The impact of different representations of droplet surface tension, including assuming $\sigma = \sigma_w$, is explored with the different thermodynamic formulations of Köhler Theory (**??**). In defining κ-Köhler Theory in Eq. (4), we have followed **?** and stated the surface tension as that of the solution droplet–air interface. A sentence has been added to clarify that $\sigma = \sigma_w$ is assumed when

inverting for κ from $D_{p,c}$ and SS_c, which is the basis for considering effects of droplet surface tension via the resulting κ values.

"Furthermore, we have assumed, for the purposes of this calculation, that $\sigma = \sigma_w$ such that any effects of changes in droplet surface tension on cloud droplet activation are captured by the evaluated effective κ parameter."

11. Page 8, line 12: Is this Dp,c the same as Dp,50? C.f. previous comments regarding activation and critical sizes.

    Yes, it has been changed to $D_{p,50}$.

12. Page 19, line 15: Do you mean Ragweed rather than poplar? The solid green curve for poplar is > k_AS for all sizes.

    Yes, the reviewer is correct.

    "For poplar, this effect is predicted to be sufficiently pronounced to make even the intrinsic hygroscopicity of the pure pollenkitt particles larger than ammonium sulfate. For ragweed, the effect is seen for the smaller particles, which activate as more concentrated droplets."

Technical comments:

1. Cloud activation is strange terminology. I suggest changing to condensation nuclei (CN) activation, or similar, throughout

   We have changed cloud activation to cloud *droplet* activation, which is the more precise term, throughout the manuscript.

2. Page 5, line 26: remove "(increasing d)"

   Done.

3. Page 8, Eq. 4: Replace M_w and rho_w with partial molar volume as in Eq.1. Then no need to redefine. R also already defined under Eq.1

   We have written κ-Köhler Theory as originally formulated by **?**. Implicit in this expression of Köhler Theory is the assumption that the droplets being considered are dilute enough such that $\nu_w = M_w/\rho_w$. This is a common assumption since ν_w is often not a known as a function of concentration, but not the general expressions of Eqs. 1 and 4.

4. Page 9, line 11: section 3.2 ?

   Yes, it has been corrected.

5. Page 11, line 5: change weight –> mass

   Done. It has also been changed in Tables 2 and 3.

6. Page 12, line 20: Define growth factor

   Done.

   "The relative diameter growth factor at the critical point of activation –the ratio of droplet size at activation to the dry particle size, here as $d_c/D_{p,50}$– decreases with particle size . . . "

7. Page 12, line 25: "high droplet total concentration", a bit confusing replace with "high total pollenkitt concentrations" or similar (if that's what you mean).

   We have attempted to clarify the sentence:

   "This effect is reducing κ values to a greater extent than any simultaneous increase in κ from reduced surface tension at the highest total solute concentrations in the droplets."

8. Page 12, line 28: nether -> neither

   Oops, thank you.

9. Figure 3: explain box whiskers in caption

   An explanation has been appended to the figure caption:

   "Error bars are standard deviations from the $D_{p,50}$ calculated from the SMCA data inversion and standard deviations from the kappa inverted from pairs of $D_{p,50}$ and SS_c."

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Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2018-394/acp-2018-394-AC1-supplement.pdf

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