

Supporting Information for "Modeling CCN activity of chemically unresolved model HULIS, including surface tension, non-ideality, and surface partitioning"

Nønne L. Prisle and Bjarke Mølgaard

July 31, 2018

S1 Model sensitivities

We have tested the sensitivity of calculations – in particular those using the comprehensive partitioning model (P) – to variation in key input parameters, including surface tension parametrization, assumed NAFA mass density and molecular weight, activation temperature, and dry particle composition. Selected results are discussed below.

S1.1 Temperature

The temperature T (Kelvin) inside the cloud condensation nucleus counter (CCNC), where particle activation is taking place and measured, depends on the supersaturation ($SS = (S - 1) \cdot 100\%$) inside the instrument, approximately according to the linear relationship (T.B. Kristensen, personal communication)

$$T = 7.4 SS + 298.75. \quad (1)$$

Over the range of particle sizes measured by Kristensen et al. (2014), the activation temperature therefore varies roughly between 298 K for the lowest supersaturations and 313 K for the highest.

In our Köhler calculations, we use a constant temperature of 303.15 K for all particle sizes to evaluate their critical supersaturations from the equilibrium Köhler curve. Temperature affects calculations both indirectly through the surface tension, which in this range increases with decreasing temperature according to Eq. 3 in Section 2.2.1, and directly through the Kelvin term of Eq. 1 in Section

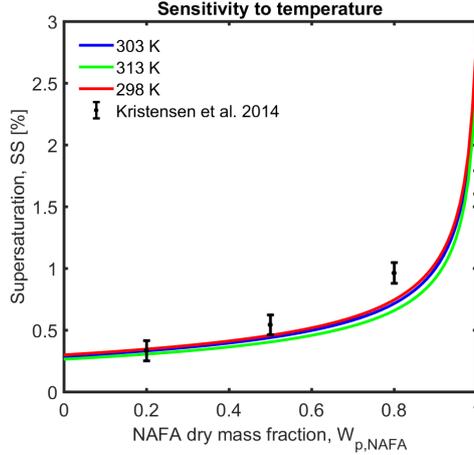


Figure S1: Sensitivity of critical supersaturations SS_c predicted with the comprehensive partitioning model (P) to temperature variations estimated inside the CCNC instrument during measurements of droplet activation.

2, which also decreases for increasing temperature. We have tested sensitivity of the (P) model to variations in temperature between 298 and 313 K. Results are shown in Fig. S1 for calculated critical supersaturations as function of 50 nm dry particle NAFA mass fraction. For lower temperatures, the calculated SS_c are slightly higher, and vice versa, as expected, but overall the temperature variation in this range has only minor influence on results.

S1.2 Assumed density of NAFA

Tracing back to experimental (mobility) diameter based particle sizing, the masses (m_i) of dry particle constituents (i) initialize the calculations of droplet growth. Given by Eq. 3 in Section 2, the assumed NAFA mass density ρ_{NAFA} affects calculations via the predicted amounts of both NAFA and NaCl solutes present in (spherical) particles of a given dry size D_p and corresponding volume. For a given particle composition in terms of relative NAFA and NaCl mass fractions $W_{p,\text{NAFA}} + W_{p,\text{NaCl}} = 1$, the volume fractions of each dry particle component $i = \text{NAFA, NaCl}$ are

$$\epsilon_i = \frac{W_{p,i}}{\rho_i} \left(\frac{W_{p,\text{NAFA}}}{\rho_{\text{NAFA}}} + \frac{W_{p,\text{NaCl}}}{\rho_{\text{NaCl}}} \right)^{-1}. \quad (2)$$

A higher mass density of NAFA therefore increases the *volume* fractions ϵ_i of both NAFA and NaCl in particles of a given dry volume and fixed relative *mass* fractions $W_{p,i}$, according to Eq. 2. It therefore affects the amounts of both soluble salt m_{NaCl}^T

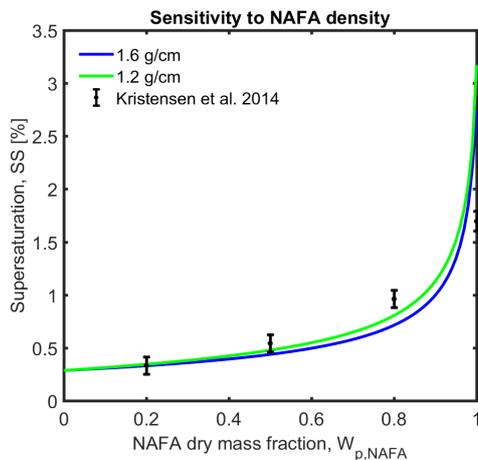


Figure S2: Sensitivity of the comprehensive partitioning model (P) to assumed mass density of NAFA for initializing Köhler calculations.

and surface active NAFA solute m_{NAFA}^T assumed to be present in the particles from the onset of droplet growth.

Figure S2 shows calculated critical supersaturations with representations (P), assuming a density for NAFA of 1.6 g cm^{-1} (base case) corresponding to a density similar to that of Suwannee River Fulvic Acid (SRFA), another common reference humic substance (Dinar et al., 2006), and 1.2 g cm^{-1} , a value similar to that assumed for the $\text{C}_8 - \text{C}_{12}$ FAS (Prisle et al., 2010, e.g. and references herein), which are significantly smaller molecular surfactants than NAFA. Due to the much higher average molecular weight measured for NAFA (Mäkelä and Manninen, 2008) than for the FAS, the value of 1.2 g cm^{-1} is believed to be a lower (and likely too low) reasonable limit for ρ_{NAFA} . The NAFA density assumption does have a small effect on calculated SS_c , with the lower density leading to higher critical supersaturations, as expected. Due to the low overall influence of NAFA on droplet activation properties, we believe the effect is in fact mostly due to smaller amounts of soluble NaCl assumed to be present in dry particles of a given size and composition, when assuming the lower density value for NAFA, as given by Eq. 2.

S1.3 Assumed molecular mass of NAFA

By using mass-based parametrizations for both surface tension and water activity, the model should in principle not need any assumptions of molecular mass M_i for dry particle constituents. However, we found that for technical reasons, an assumption of M_{NAFA} is still needed to augment calculations of gradients for droplet properties. Specifically, bulk–surface partitioning equilibrium is iterated in

terms of NAFA molecular numbers, which are then converted back to mass via the assumed molecular mass. Due to the very high average molecular mass of NAFA, combined with the mixture’s significant impact on surface tension, the partitioning of a single NAFA molecule in a few cases affects the outcome of calculations. This specifically happens for the smallest particles with the highest NAFA fractions W_{NAFA} , which activate as very small and highly bulk-depleted droplets. The average molecular mass of NAFA was measured by Mäkelä and Manninen (2008) as 4266 g mol^{-1} , within a distribution, whereas those of SRFA (Dinar et al., 2006) and of atmospheric HULIS (Kiss et al., 2003) have been estimated to be considerably lower. We have tested the sensitivity of calculations with representation (P) to decreasing the assumed NAFA mass density to $2000 - 1000 \text{ g mol}^{-1}$ and, as a representative value for SRFA and atmospheric HULIS average molecular mass, and as an absolutely lowest bound of NAFA average molecular mass, to 500 g mol^{-1} . Results are shown in Fig. S3 for SS_c as a function of 50 nm dry particle composition. The difference between 500 and 4266 g mol^{-1} represents a dramatic change in assumed NAFA properties and for particles with NAFA mass fractions above about 80%, it does influence calculated activation properties. The effect is much less pronounced for larger particles, but for consistency with other results presented, and to highlight the largest differences possible, results are here shown for the most sensitive small particle sizes. Experimental values from Kristensen et al. (2014) for particles with approximate dry sizes of 50 nm are shown for reference. We speculate that a more modest difference in NAFA molecular mass, if there were such a difference between the samples measured by Mäkelä and Manninen (2008) and Kristensen et al. (2014), or a similar variation within a given NAFA sample used in experiments, in principle could reconcile calculations using (P) with experimental SS_c via a similar computational mechanism. We however also note that the reported uncertainty on measured NAFA SS_c in terms of experimental standard deviations is low, and the influence on sample variability on results therefore cannot be very large.

S1.4 Surface tension parametrization

Models (P) and (B) include concentration dependent droplet surface tension and we tested the sensitivity of calculations to the functional form of the ternary surface tension fit, as well as of the fitting parameters $q_{\text{st}1}$ and $q_{\text{st}2}$. Eq. 3 in Section 2.2.1 accounts implicitly for the effect of NaCl on surface tension via the dependence on fitting parameters on solute mixing ratio w_{NAFA} , as given by Eqs. 4 and 5 in the same section. We also used a ternary parametrization with explicit account

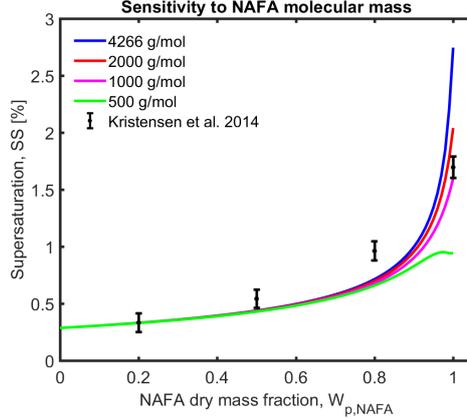


Figure S3: Sensitivity of the comprehensive partitioning model (P) to estimated average values of NAFA molecular mass affecting iterations of the NAFA partitioning equilibrium in droplets during activation, via the Köhler equation.

for NaCl via an additional binary salt term

$$\sigma = \sigma_w + \left(\frac{d\sigma_{\text{NaCl}}}{dc_{\text{NaCl}}} \right) c_{\text{NaCl}} - q_{\text{st1}} \ln(1 + C_{\text{NAFA}}/q_{\text{st2}}), \quad (3)$$

with fitting parameters

$$q_{\text{st1}} = 9.995 - 4.259w_{\text{NAFA}} - 0.03879w_{\text{NAFA}}^2 \quad (4)$$

and

$$q_{\text{st2}} = 0.5919 - 0.432w_{\text{NAFA}} + 0.1175w_{\text{NAFA}}^2. \quad (5)$$

Here, c_{NaCl} is the salt molal concentration in $\text{mol}(\text{kgwater})^{-1}$, C_{NAFA} is the NAFA mass concentration in g L^{-1} , and the binary NaCl surface tension gradient $\frac{d\sigma_{\text{NaCl}}}{dc_{\text{NaCl}}} = 1.61 \text{ mN m}^{-1}/\text{mol}(\text{kg water})^{-1}$ is calculated from data from Low (1969) as was done by Prisle et al. (2010).

For the present cases, model calculations are somewhat sensitive to the functional form of the surface tension parametrization and fitting parameters. We therefore also tested Eq. 3 with a different set of quadratic parameters, $q_{\text{st1}} = 72.13 - 158.4w_{\text{NAFA}} + 93.52w_{\text{NAFA}}^2$ and $q_{\text{st2}} = 6.556 - 15.51w_{\text{NAFA}} + 9.431w_{\text{NAFA}}^2$. Results are qualitatively similar and only shown for parameter values in Eqs. 4 and 5. Model sensitivity is greater for (P), where critical droplets are more concentrated and with bulk solute compositions w_i which are dramatically changed from the nominal dry particle compositions $W_{p,i}$. For these droplets, the surface tension equation is extrapolated far outside the range of compositions constrained by data

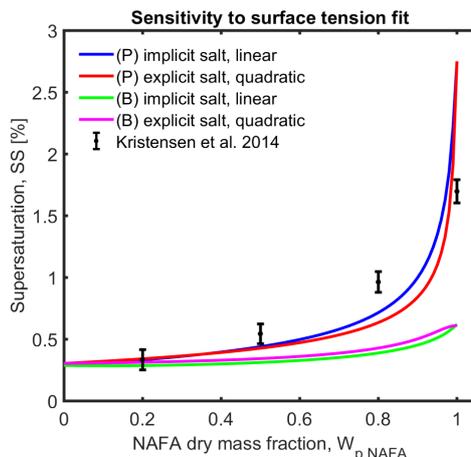


Figure S4: Sensitivity of Köhler model frameworks (P) and (B) to fitting equations for ternary surface tension, including implicit and explicit binary salt term, and linear and quadratic equations for the Szyszkowski surface tension parameters.

and the validity of the explicit salt term and accompanying fit parameter values is not readily confirmed. Model framework (B) is less sensitive to the ternary fit equation, as droplets are more dilute, but notably have compositions much better constrained by the data underlying the fits. Using the explicit salt terms lead to slightly higher predicted critical supersaturations, but notably far from able to reconcile the severe underestimations of SS_c generally observed with (B).

S1.5 Small amounts of impurities in NAFA

Small amounts of soluble impurities can significantly enhance organic aerosol CCN activity, from increased hygroscopic properties of the overall particle (Bilde and Svenningsson, 2004). We tested the sensitivity of each of the four model representations to the assumption of 3 and 5% NaCl impurity present in the NAFA sample. Results are shown in Fig. S5 against the corresponding calculations assuming 100% NAFA (base case) and experimental values from Kristensen et al. (2014) for pure NAFA particles. For representation (S), calculations are not feasible for pure NAFA and have therefore been made for 99% instead. Indeed, a relatively small amount of only 3% NaCl essentially reconcile both the partitioning model (P) and the simple representation (S) with experimental values. For mixed NAFA–NaCl particles, change of composition from the nominal value could arise not only from an actual contamination or deterioration of the NAFA sample measured, but also from fractionation during particle production for measurements changing dry particle composition from that of the solute in the solution from which particles

were generated. Such a phenomenon was observed by Brooks et al. (2004) for organic–inorganic mixtures. We note that the size dependency of our calculations have a slightly different slope than the actual data and assuming a 3% NaCl impurity leads to slight underestimations of critical supersaturations for the smallest particles and conversely to slight overestimations in the high particle size end. A composition fractionation as reported by Brooks et al. (2004) could very well vary in degree with the size of the particles produced, with smaller particles less depleted or even enriched in the surface active component, since these particles are also created from smaller nebulized droplets. This would explain the observed relative trends.

References

- Bilde, M. and Svenningsson, B.: CCN Activation of Slightly Soluble Organics: The Importance of Small Amounts of Inorganic Salt and Particle Phase, *Tellus*, 56B, 128–134, 2004.
- Brooks, S. D., DeMott, P. J., and Kreidenweis, S. M.: Water uptake by particles containing humic materials and mixtures of humic materials with ammonium sulfate, *Atmospheric Environment*, 38, 1859–1868, 2004.
- Dinar, E., Mentel, T. F., and Rudich, Y.: The density of humic acids and humic like substances (HULIS) from fresh and aged wood burning and pollution aerosol particles, *Atmospheric Chemistry and Physics*, 6, 5213–5224, 2006.
- Kiss, G., Tombacz, E., Varga, B., Alsberg, T., and Persson, L.: Estimation of the average molecular weight of humic-like substances isolated from fine atmospheric aerosol, *Atmospheric Environment*, 37, 3783–3794, 2003.
- Kristensen, T. B., Prisle, N. L., and Bilde, M.: Cloud droplet activation of mixed model HULIS and NaCl particles: Experimental results and κ -Köhler theory, *Atmospheric Research*, 137, 167–175, 2014.
- Low, R.: A Theoretical Study of Nineteen Condensation Nuclei, *Journal de Recherches Atmospheriques*, pp. 65–78, 1969.
- Mäkelä, J. and Manninen, P.: Molecular size distribution and structure investigations of humic substances in groundwater, working report 2008-36, Posiva Oy, Posiva Oy, Olkiluoto, FI-27160 Eurajoki, Finland, 2008.
- Prisle, N. L., Raatikainen, T., Laaksonen, A., and Bilde, M.: Surfactants in cloud droplet activation: mixed organic-inorganic particles, *Atmos. Chem. Phys.*, 10, 5663–5683, <https://doi.org/10.5194/acp-10-5663-2010>, 2010.

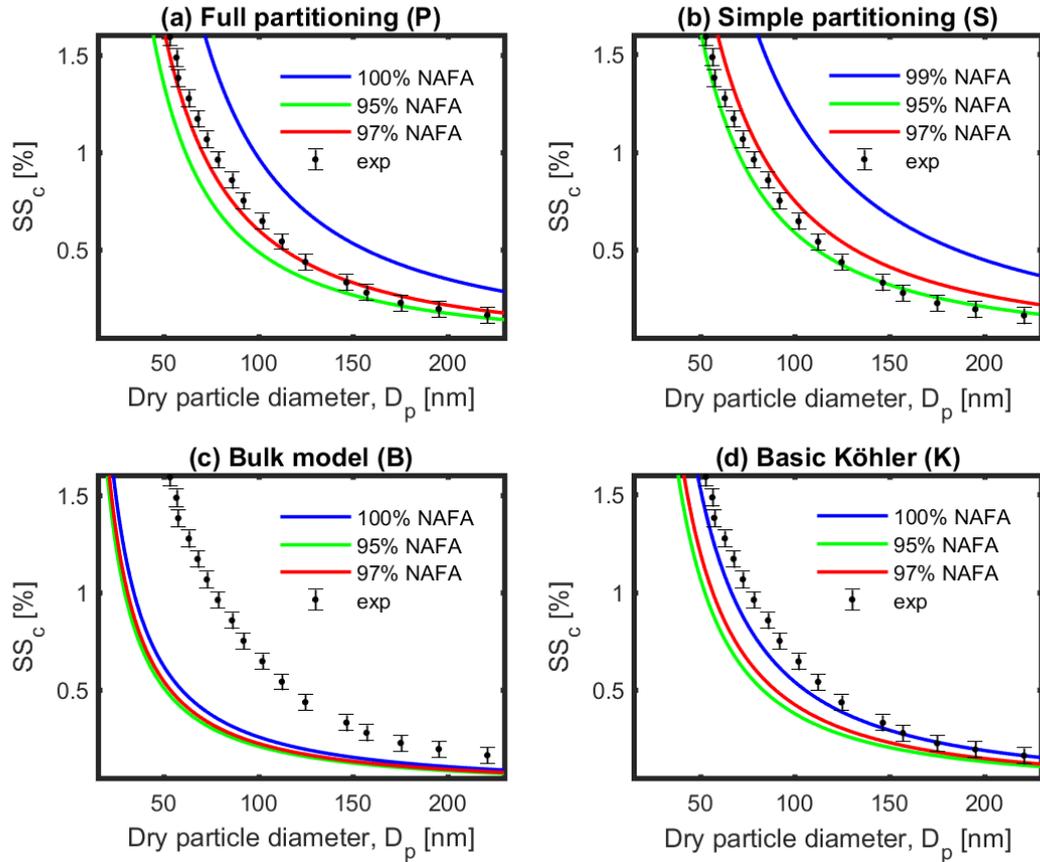


Figure S5: Sensitivity of the model calculations to small amounts of impurities in the NAFA sample, exemplified by 3% and 5% by mass of NaCl in nominally pure NAFA particles. Each panel shows results for one of the four different surfactant CCN activity representations, (a) the comprehensive partitioning model (P), (b) simple partitioning (S), (c) bulk solutions properties (B) and (d) basic Köhler theory (K). As representation (S) cannot be applied for pure NAFA particles, calculations with 99% NAFA are therefore shown instead.