CCN activity of six pollenkitts and the influence of their surface activity

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Abstract. Pollenkitt is a viscous material that coats grains of pollen and plays important roles in pollen dispersion and plant reproduction. It may also be an important contributor to pollen water uptake and CCN activity. The chemical composition of pollenkitt varies between species, but has been found to comprise complex organic mixtures including oxygenated, lipid, and aliphatic functionalities. The mix of functionalities suggests that pollenkitt may display aqueous surface activity, which

5   could significantly impact pollen interactions with atmospheric water. Here, we study the surface activity of pollenkitt from six different species and its impact on pollenkitt hygroscopicity. We measure cloud activation and concentration dependent surface tension of pollenkitt and its mixtures with ammonium sulfate salt. Experiments are compared to predictions from several thermodynamic models, taking aqueous surface tension reduction and surfactant surface partitioning into account in various ways. We find a clear reduction of surface tension by pollenkitt in aqueous solution and evidence for impact of both

10   surface tension and surface partitioning mechanisms on cloud activation potential and hygroscopicity. In addition, we find indication of significant impact of complex non-ideal solution effects in systematic and consistent size dependency of pollenkitt hygroscopicity.

1 Introduction

Pollen is the male gametophyte of seed plants and plays a critical role in plant reproduction (Punt et al., 2007). Pollen grains can

15   disperse in air and adhere on insects or other animals allowing for their distribution over large areas (Bedinger, 1992; Pacini, 2010). Pollen possesses a range of ornamentations that vary in morphology (i.e., spherical, granulate, reticulate, and echinate) and feature size, with nominal particle diameters of 3-250 μm. Pollen of entomophilous and zoophilous species are coated by a viscous material that enables numerous functions, including adhesion and transport by pollinators (Pacini and Hesse, 2005). This substance, typically called pollenkitt, is formed from the final degradation of the plant tapetum during pollen development, resulting in the deposition of a coating rich in plastid-derived lipids and other pigmented compounds (Pacini, 1997; Dickinson

et al., 2000; Knoll, 1930). Pollen transmission is facilitated by the ability of pollenkitt to adhere pollen grains to one another and to pollinators during transport.

5   While the chemical composition of pollenkitt has been characterized in a number of studies (Piffanelli et al., 1998), relatively little is known about its physico-chemical properties. Pollenkitt is comprised of a mixture of saturated and unsaturated lipids, carotenoids, flavonoids, proteins, and carbohydrates (Piffanelli et al., 1998; Pacini and Hesse, 2005; Dobson, 1988). Analysis of the lower molecular weight compounds from the pollenkitt of *Rosa rugosa* revealed aromatics, C11-C16 aliphatics, terpenoids, and C16 acetate, with few of these compounds also found in *Rosa canina* (Dobson et al., 1987). From a collection of pollen
10   from 69 angiosperms, Dobson (1988) found the pollenkitt to contain non-glyceride neutral lipids (hydrocarbons, fatty acid methyl esters, sterol esters, aldehydes, and ketones), a few polar lipids, and pigments (yellow carotenoids and flavonoids).

    Interestingly, in pollen from some plant species the pollenkitt serves as a barrier to reduce the rate of water loss, preserving the viability of the pollen, which decreases with dehydration (Pacini and Hesse, 2005). The polar components in pollenkitt should support some absorption of water, and many of these substances are expected to be water soluble themselves. Previ-
15   ous quantitative studies of pollen adhesion to varied surfaces by atomic force microscopy (AFM) (Lin et al., 2013) showed that pollenkitt significantly enhances pollen adhesion and that the effect was driven by the formation of pollenkitt capillary bridges. A subsequent study found that pollenkitt hydration by water uptake at high humidity changed pollenkitt properties and its capillary adhesion (Lin et al., 2015). This finding has important implications for understanding pollenkitt's role in plant reproduction, allergy and asthma, and pollen as atmospheric condensation nuclei.

20   The hygroscopic water uptake of whole pollen grains was studied by Pope (2010) and Griffiths et al. (2012) who found that pollen of six different species were moderately hygroscopic with water-wettable surfaces. Using an electrodynamic balance, Pope (2010) determined values for the hygroscopicity parameter κ to be between 0.05 and 0.1 for four different types of pollens (daffodil, water birch, pussy willow, and black walnut), while Griffiths et al. (2012) found κ values between 0.08 and 0.17 for six different pollens (rye, firebush, giant sage, daffodil, water birch, and pussy willow.) Due to their large grain
25   sizes, they concluded that pollen grains would be effective CCN, even at low supersaturations. However, suspended number concentrations of whole pollen grains are often too low to expect significant impact on cloud microphysics. Steiner et al. (2015) characterized the cloud forming potential (CCN activity) of so-called submicron subpollen particles (SSP), which form as fragments when whole pollen grains uptake water and burst at high ambient relative humidities. They found such SSP of six pollen types characteristic of mid-latitudes to be active enough to act as CCN, with particles of 200-250 nm diameters
30   activating at atmospheric conditions below 1% supersaturation. From these studies, it is unclear how much of the observed hygroscopicity of pollen is driven by water adsorption onto the insoluble surfaces vs. water uptake by the pollenkitt coatings. Here, we focus on understanding the water-uptake properties of the pollenkitt mixture specifically.

    Depending on the thickness of its pollenkitt coating, the water uptake properties of a pollen particle depend on the ability of the pollenkitt mixture to depress water activity through solute and surface tension effects. Based on the current knowledge of
35   pollenkitt chemical composition, comprising a suite of organic compounds with both hydrophilic and hydrophobic moieties, we might expect the pollenkitt mixture to exhibit some degree of both solubility and surface activity in aqueous solution, analogous to e.g. secondary organic aerosol (SOA) (McNeill et al., 2014). Surface tension depression from organic surfactants has been

recognized to impact cloud forming potential of organic aerosol predicted from equilibrium Köhler theory. Early work by e.g. Shulman et al. (1996) and Facchini et al. (1999, 2000) neglected the mass balance of surfactants assumed to be contained in the

5 aerosol during their bulk-to-surface partitioning. Later work recognized this limitation (Sorjamaa et al., 2004) and subsequent studies for model atmospheric aerosol systems comprising fatty acids (Prisle et al., 2008, 2010b), model-HULIS (Kristensen et al., 2014), and organo-sulfates (Hansen et al., 2015), demonstrated how surface activity and its effect on CCN activity involves complex interactions between both surface tension and bulk-to-surface partitioning. As a result, the overall impact of surfactants on atmospheric cloud droplet formation is difficult to quantify in a straightforward manner (Prisle et al., 2012). Two

10 factors must be highlighted in this context. First, it is still not possible to directly measure the surface tension of dilute aqueous submicron activating droplets containing surfactants, and all modeling is thus based on downscaling macroscopic, or bulk phase, measurements to droplet size systems using thermodynamic relations (e.g. Prisle et al., 2008, 2010b; Topping, 2010; Raatikainen and Laaksonen, 2011). Measurements that have been able to directly measure interfacial tensions using optical tweezers (Bzdek et al., 2016) or biphasic microfluidic devices (Boyer and Dutcher, 2017) have relied on optical techniques that

15 require studying droplets larger than the typical size of an activated droplet. Second, detailed characterization of the impact of surface activity on droplet activation thermodynamics has to date only been made for a small ensemble of organic aerosol systems, with limited chemical complexity (Petters and Petters, 2016). Gas-phase compounds may also act as surfactants (Romakkaniemi et al., 2011; Sareen et al., 2013), further complicating the potential interactions that occur in atmospherically-relevant systems.

20 Recent work suggests that there may indeed be a suite of aerosol systems for which the impact of droplet surface tension at the point of activation could be more significant than we have previously found. Padró et al. (2007) proposed using so-called Köhler Theory Analysis (KTA) derived from simple Köhler theory to infer average values of surface tension and bulk molar volume of an aerosol system with known and systematic perturbations on the composition, usually by adding a known amount of electrolyte to an unknown organic mixture. Other work focused on more comprehensive approaches for thermodynamically

25 consistent predictions of these properties (Prisle et al., 2008, 2010b, e.g.). Based on results from these comprehensive models, Prisle et al. (2011) subsequently proposed a simple representation of the overall CCN activity of surface active organic aerosol to facilitate a computationally efficient approach to study larger-scale effects. The simple approach essentially assumes an effective hygroscopicity value (Petters and Kreidenweis, 2007) of zero for the surfactant. In global predictions of cloud droplet numbers and cloud radiative forcing, the resulting effect of surface activity was therefore found to be negligible (Prisle

30 et al., 2012). Ruehl et al. (2016) found that a framework based on very similar assumptions to those of Prisle et al. (2011) demonstrated that surface tension could enhance droplet hygroscopicity and CCN activation significantly. Ovadnevaite et al. (2017) showed that there may be evidence for such mechanisms in observations from oceanic locations, with potential global implications due to the relative significance of marine aerosol.

Pollenkitt represents a potentially exciting new class of surface-active atmospheric organics with complex chemical functionalities. Here we study the potential for six different pollenkitts to reduce aqueous surface tension and promote water uptake on pollen for a wide range of humidities.

2 Methods

2.1 Pollenkitt sample preparation

5 Pollenkitts were obtained from the pollen grains of six different species, including olive (*Olea europaea*), black poplar (*Populus nigra*), Kentucky bluegrass (*Poa pratensis*), common ragweed (*Ambrosia artemisiifolia*), common dandelion (*Taraxacum officinale*), and common sunflower (*Helianthus annuus*), as previously studied at subsaturated conditions (except Kentucky bluegrass) by Lin et al. (2013). All the native non-defatted pollen grains were purchased from Greer Laboratories (Lenoir, NC), stored at 0 °C, and were used as received without further purification. In the case of the dandelion pollen, the pollen

10 grains were obtained off of honey bees instead of the flowers directly so that the dandelion sample includes some amount of nectar (sugars dissolved in water) from the honey bees (Sladen, 1912; Campos et al., 2008). The extraction of pollenkitt from each native pollen grain was performed by adding a known mass of each pollen sample to 40 mL deionized (DI) water and shaking by a rotational shaker (Barnstead Thermolyne Labquake Shaker Rotisserie) for 10-15 min. Then the solutions were centrifuged (2.7×1000 rpm, 20 min) in an IEC Centra CL2 centrifuge (Thermo Scientific) and subsequently filtered to re-

15 move all the pollen particles. The resulting solutions were diluted with DI water to concentrations suitable for the appropriate CCN and surface tension measurements. Solutions were prepared such that the extracted amount of pollenkitt was completely dissolved in the aqueous solution and no phase separation was observed. Surface tension measurements were made over a pollenkitt concentration range of 0.01–200 mg L^{-1}. CCN measurements were made at pollenkitt concentration of 0.05 mg L^{-1}, except for olive pollenkitt which was made at 0.5 mg L^{-1}.

20   Size-resolved CCN activity of pollenkitt and their mixtures with ammonium sulfate (AS) was measured using Scanning Mobility CCN Analysis (SMCA; Moore et al., 2010). A schematic and flow diagram of the experimental setup for CCN activation experiments, closely resembling that used here, is presented by (Padró et al., 2007). At the time of each experiment, prepared 50 mL aqueous samples were transferred to a large volume nebulizer (Hudson RIC, Ref. 1770). Filtered laboratory air was pumped into the nebulizer at 5 psig with the nebulizer set to a flow rate of 10 L min^{-1} and 98% O$_2$. The generated

25 particles were dried to roughly 10% RH in two diffusion driers and charged neutralized (TSI 3077) before being sent to a differential mobility analyzer (DMA, TSI 3080). The DMA voltage is continuously cycled to sample particles sizes in the range of 7-512 nm over 135 s. The size-classified aerosol is split between a condensation particle counter (TSI CPC 3010) to measure total particle number and a cloud condensation nuclei counter (Droplet Measurement Technologies CCN-100) to measure activated particle number as a function of supersaturation. An inversion procedure is used to calculate the fraction of

30 total particles at a given size that have activated into droplets (Moore et al., 2010). For each DMA size distribution, these data are fit to a sigmoidal function after correcting for diffusional losses and multiply-charged particles in the DMA. The particle dry diameter at which 50% of the particles activate into droplets is the dry diameter corresponding to a particle with critical supersaturation equal to the instrument supersaturation. The CCN counter was operated at nine different supersaturations from 0.1 to 1.5% for 20 minutes each so that approximately eight complete size distributions from the DMA are sampled at each supersaturation. Particle number concentrations introduced to the CCN counter were less than 1000 cm^{-3} to avoid water vapor depletion effects in the CCN counter (Lathem and Nenes, 2011).

2.2 Surface tension measurements

5 In order to investigate the specific impact of surface tension on pollenkitt CCN activation, we measured concentration-dependent surface tension of two of the investigated pollenkitts in their pure aqueous solutions and in aqueous solution with ammonium sulfate (AS) in a mass ratio of 4:1, so that AS comprise 20% of the total solute mass. Ammonium sulfate was selected as a well-characterized proxy for the inorganic fraction of atmospheric aerosol, and we focused on poplar and ragweed pollenkitt as the most and least CCN active of the six pollenkitts investigated (see Section 3.1 below).

10 Surface tension of binary and ternary aqueous pollenkitt solutions were measured via axisymmetric drop shape analysis of pendant drops in air with a ramé-hart goniometer (Model 250). Briefly, a pendant drop of solution was created by using a syringe with a steel needle, and a charge-coupled device (CCD) camera captured the variation of drop shape. The surface tension was obtained by analyzing the contour shape resulting from the balance of gravitational and surface forces through solution of the Young-Laplace equation as described elsewhere (Berry et al., 2015). All experiments were performed at room

15 temperature of 21 °C.

Samples for surface tension measurements were prepared in the same way as for CCN measurements described above. Concentrations ranged from 0.01-200 mg pollenkitt per L solution, all of which were observed during sample preparations to be within the aqueous solubility range of each pollenkitt.

2.3 Köhler modeling

20 Cloud droplet activation of pollenkitt particles was modeled using different models previously developed by Prisle and co-workers. All models are based on equilibrium Köhler theory in the form

$$S \equiv \frac{p_w}{p_w^0} = a_w \exp\left(\frac{4\nu_w\sigma}{RTd}\right) \tag{1}$$

where p_w is the equilibrium water partial pressure over an aqueous droplet, p_w^0 is the saturation vapor pressure of pure water at the temperature T (in Kelvin) in question, S is equilibrium water vapor saturation ratio for the stable droplet, a_w is the

25 water activity of the solution droplet, ν_w is the partial molar volume of water in this solution, σ is the droplet surface tension, R is the universal gas constant, and d is the spherical solution droplet diameter. For growing droplets (increasing d), the equilibrium Köhler curve and threshold for droplet cloud condensation nucleus (CCN) activation, the critical saturation ratio (S_c) and corresponding critical droplet diameter (d_c), are iterated for each dry particle size and composition (pollenkitt, PK, or pollenkitt mixtures with ammonium sulfate, PK–AS). Droplets that have been exposed to ambient water saturation ratios

30 larger than their respective threshold values $(S \geq S_c)$, and thus surpassed their critical diameters $(d \geq d_c)$, are assumed to be activated cloud droplets.

We use four different Köhler models, each based on a different set of assumptions regarding surface tension and the bulk-to-surface partitioning of the surface active species–pollenkitt, in this case–in aqueous solution. The three thermodynamically consistent models developed in previous work (Prisle et al., 2008, 2010b) and described in detail therein are:

1. The most comprehensive full partitioning model, which explicitly iterates the bulk-to-surface partitioning of surface active species at every aqueous droplet size and dilution state, and evaluates droplet surface tension based on the resulting bulk solute concentrations and surface excess of the partitioning equilibrium.

2. The bulk aqueous solution model, where depletion effects of bulk-to-surface partitioning of surface active species on the bulk composition are neglected, and droplet surface tension is evaluated based on the total solute concentrations in aqueous solution.

3. The constant surface tension of pure water model, where surface activity of any droplet component is neglected, such that the droplet bulk concentrations of all solutes is assumed directly given by the total droplet composition, and reduction of aqueous surface tension from that of pure water is neglected.

In each of these models, the impact of solute specific interactions of pollenkitt and ammonium sulfate on water activity is neglected, i.e. $a_w \equiv \gamma_w x_w \approx x_w$, where x_w is the mole fraction concentration of water in solution. This is done due to lack of information of the respective activity coefficients and their concentration dependence in solution, but as we discuss below, it may not always be a fully sufficient assumption.

We also used the simple partitioning scheme introduced by Prisle et al. (2011), where the bulk-to-surface partitioning of surface active species is essentially taken to the extreme, such that the droplet bulk is entirely depleted of surfactant species, with resulting concentration $c_{PK}^B = 0$. This implies that both the effective hygroscopicity parameter (see Section 2.5) of pollenkitt in the droplets and the droplet surface tension reduction from the pure water value vanishes, i.e. $\kappa_{PK} = 0$ and $\sigma = \sigma(c_{PK}^B = 0) = \sigma_w$ according to Equation 3 (see Section 2.4). The resulting droplet bulk solution consists of binary aqueous ammonium sulfate. The impact of AS dissociation and its ions on water activity is accounted for using a parametrization (Prisle, 2006) based on data from Low (1969). The simple partitioning model was previously shown to work well for predicting the impact of strong surfactants on CCN activity of mixed surfactant–salt model particles comprising sodium dodecyl sulfate (SDS) and the atmospheric fatty acid salts decanoate and dodecanoate. However, it works less well for sodium octanoate, which is comparatively less surface active (Prisle et al., 2011).

Common for all models, we need to determine the total amount of pollenkitt and ammonium sulfate solute in the aqueous droplet phase. For these calculations, the initially dry particles are assumed to be spherical with volume-equivalent diameters corresponding to the electrical-mobility diameter mode selected by the DMA during experiments, $D_p^e = D_p$ (Sorensen, 2011). Although pure AS particles have been observed to have shape factors of 1.04, we here assume that the fraction of organic component is too high to support AS crystal structure and particles are assumed to be spherical. The dry particle volume, which determines the amount of solute in the growing droplets, is then obtained as $V_p = \frac{\pi}{6} D_p^3$. Furthermore, we then need to know the dry particle mass density ρ_P and the molecular weights M_i of all particle components. We assume volume additivity of the various chemical components in the dry particles as

$$\rho_{p,add} = \left(\sum_i \frac{W_{p,i}}{\rho_i} \right)^{-1}, \tag{2}$$

Table 1. Main assumptions regarding surface tension (σ), bulk-to-surface (B–S) partitioning, and water activity, in terms of the mole fraction based water activity coefficient γ_w ($a_w = \gamma_w x_w$), in the four Köhler models used.

Model	B–S partitioning	σ reduction	γ_w
partitioning	yes, conc. dep.	yes	1
bulk	no	yes	1
water	no	no	1
simple	yes, complete	no	$\frac{1}{x_w}\left(1 - 0.039767 b_{AS} + 0.0079808 b_{AS}^2 - 0.0022641 b_{AS}^3\right)$ (Prisle, 2006)

where $W_{p,i}$ is the dry particle mass fraction and ρ_i the bulk mass density of each individual component i, respectively. The density of ammonium sulfate is well-known with $\rho_{AS} = 1.769$ g cm^{-3}. For organic aerosol mixtures, a range of densities has been measured in the atmosphere, often between 1.2 and 1.7 g cm^{-3} (Hallquist et al., 2009), but significantly lower values have also been found (Kannosto et al., 2008). The individual components of organic aerosol (OA) and their respective bulk material properties, including mass densities, often remain unknown and one approach has been to assume unit density for these compounds and their mixtures ($\rho_{OA} = 1$ g cm^{-3}) while awaiting future findings (Prisle et al., 2010a). The pollenkitts investigated here are all complex mixtures of a suite of different organic compounds. For the Köhler model calculations, we therefore initially varied mass densities of each pollenkitt organic mixture between 0.8 and 1.2 g cm^{-3}. In all cases, the higher mass densities give better agreement with measured CCN activities, and only results for those conditions are shown here. We then used Köhler Theory Analysis (KTA; Padró et al., 2007) to estimate the average effective molecular weight of each pollenkitt mixture, consistent with a mass density of 1.2 g cm^{-3} and a range of approximate surface tensions, as will be discussed further in the Results section below. An overview of the assumptions distinguishing the four Köhler models is given in Table 1. A schematic of the four Köhler models is given it Figure 1 of Prisle et al. (2012).

2.4 Surface tension parametrization

In model calculations where the impact of pollenkitt on droplet surface tension is taken explicitly into account, surface tension is evaluated from a parametrization based on the Szyskowski-Langmuir equation (Szyskowski, 1908) in the form

$$\sigma = \sigma_w + \left(\frac{d\sigma_{AS}}{dc_{AS}}\right)c_{AS} - a\ln\left(1 + \frac{c_{PK}}{b}\right). \tag{3}$$

Here, c_{AS} and c_{PK} are the mass concentrations (g solute per L of solution) of ammonium sulfate (AS) and pollenkitt (PK), respectively, and $\sigma_w = 72.2$ mN m^{-1} is the surface tension of pure water at 296.65 K. The measured surface tensions for bulk aqueous solutions of each pollenkitt were fitted to Equation 3. The surface tension gradient for binary aqueous AS, $\left(\frac{d\sigma_{AS}}{dc_{AS}}\right) = 0.01655$ mN m^{-1}/g L^{-1} was obtained by linear fitting to the data from Low (1969). The fitting parameters a and b in Equation 3 have dimensions of mN m^{-1} and g L^{-1}, respectively. Note that this fit is only pseudo-ternary, since the relative

ratio of pollenkitt and ammonium sulfate solute does not change in the solutions measured. Implications of this are discussed in the Results section below.

2.5 κ values

The relationship between particle dry diameter and CCN activity can be parameterized using a single hygroscopicity parameter (Petters and Kreidenweis, 2007). The parameter, κ, is defined based on standard Köhler theory in the form

$$S(d) = \frac{d^3 - D_p^3}{d^3 - D_p^3(1-\kappa)} \exp\left(\frac{4\sigma M_w}{RT\rho_w d}\right), \tag{4}$$

where, analogous to Equation 1, $S(d)$ is the saturation ratio over an aqueous solution drop with size d, D_p is particle dry diameter, σ is the droplet surface tension, M_w is the molecular weight of water, R is the universal gas constant, and ρ_w is the density of water.

Pairs of critical dry diameter $D_{p,c}$ and critical supersaturation SS_c values from SMCA experimental data and modeling data are used to calculate κ from Equation 4. Both κ and d are varied independently in order to minimize the difference between the theoretical and measured supersaturation (Rose et al., 2010). This was done because the simplified relations provided by Petters and Kreidenweis (2007) are only valid for $\kappa > 0.2$, a condition which is often not met by our measurements, as seen in Section 3. For measurements of each pollenkitt and pollenkitt-ammonium sulfate mixture, averages and standard deviations in κ are calculated for each supersaturation and across all supersaturations.

3 Results

Table 2. Pollenkitt CCN activity: Slope of the $\ln D_{p,50}$ vs. $\ln SS$ plot and average hygroscopicity value κ for each particle composition.

Sample	$\ln-\ln$ slope	χ^2	κ
Dandelion	-1.50±0.0299	0.01729	0.19±0.0162
Kentucky bluegrass	-1.49±0.0237	0.01105	0.21±0.0162
Olive	-1.44±0.0298	0.01873	0.17±0.0219
Poplar	-1.41±0.0308	0.02094	0.24±0.0334
Ragweed	-1.44±0.0355	0.02665	0.14±0.0203
Sunflower	-1.48±0.0339	0.02309	0.15±0.0159
Poplar + 20 wt% AS	-1.85±0.0900	0.07368	0.22±0.0739
Ragweed + 20 wt% AS	-1.63±0.0133	0.1920	0.28±0.0978

3.1 Pollenkitt CCN activity

Measured CCN activity, given as particle critical diameter ($D_{p,50}$) vs. supersaturation (SS), for the six different pollenkitts and the two mixtures with ammonium sulfate is shown in Figure 1. All the pure pollenkitts exhibit similar CCN activity, with some moderate variations between different species. Overall, the CCN activity of the six pollenkitts increase in the order ragweed $\approx$ sunflower < olive < dandelion < Kentucky bluegrass < poplar at a supersaturation of 1.0, and ragweed < sunflower < olive < dandelion < poplar < Kentucky bluegrass at a supersaturation of 0.2. See panel (a) in Figure 1. Hence, the order of increasing CCN activity varies only little with particle supersaturation and thus size.

For each particle composition, linear fits have been made to the plots of $\ln D_{p,50}$ vs. $\ln SS$. According to standard equilibrium Köhler theory, the slope of these lines should ideally be $-3/2$, and any deviations from this value would indicate the presence of size-dependent variation in particle CCN activation (albeit not which underlying size-dependent property is responsible for the variation). In cases such as this, where the well-constrained laboratory generated particle composition can be assumed to be the same for particles of all sizes, a size-dependent variation in CCN activity could result from either aqueous solubility effects in the bulk or surface tension effects on the surface.

Fitted slope values with standard deviations and goodness of fit, $\chi^2 = \sum_i (O_i - E_i)^2$ are given in Table 2. The goodness of fit is the sum of differences between observed outcomes O_i and expected outcomes E_i. For dandelion, Kentucky bluegrass, and sunflower, we see no significant deviation from a slope of $-3/2$, and thus no immediate indication in our data of size-dependent variations in CCN activity of these pure pollenkitts. For olive, poplar, and ragweed, the slopes deviate from $-3/2$ beyond the standard deviation of the fit. If size-dependent CCN activity effects are introduced by pollenkitt surface activity, we would therefore expect to find them specifically for these pollenkitts among our samples. Of these, the deviation is strongest for poplar, which is also the most CCN active pollenkitt over most of the particle size range studied. Ragweed is the least CCN active of the six pollenkitts, and has a slope similar to that of olive. We therefore chose to study possible effects of surface tension closer for the cases of ragweed and poplar pollenkitts (see Section 2.3).

For pollenkitt and ammonium sulfate mixtures (panel (b) in Figure 1), ammonium sulfate enhances CCN activity of ragweed, as might immediately be expected upon addition of a highly hygroscopic salt. However, for poplar, the enhancement of CCN activity is only seen for larger particles, whereas CCN activation is suppressed for smaller particles. In case of both mixtures, the slope of the $\ln D_{p,50}$ vs. $\ln SS$ plots change significantly compared to the respective pure pollenkitt particles. This indicates the presence of now significant size-dependent effects on CCN activity introduced by the interaction between pollenkitt and the inorganic salt via either solubility or surface tension effects.

3.2 Pollenkitt surface activity

Measured surface tension for ragweed and poplar pollenkitts and their mixtures with ammonium sulfate are shown in Figure 2. Error bars shown on the plot represent standard deviations calculated from independent measurements of three droplets. The resulting fitting parameters a and b in Equation 3 are given in Table 3. Both pollenkitts are moderately strong surfactants and able to reduce aqueous surface tension to values below 50 mN m^{-1} at concentrations of about 0.1 g L^{-1}. Below, we infer
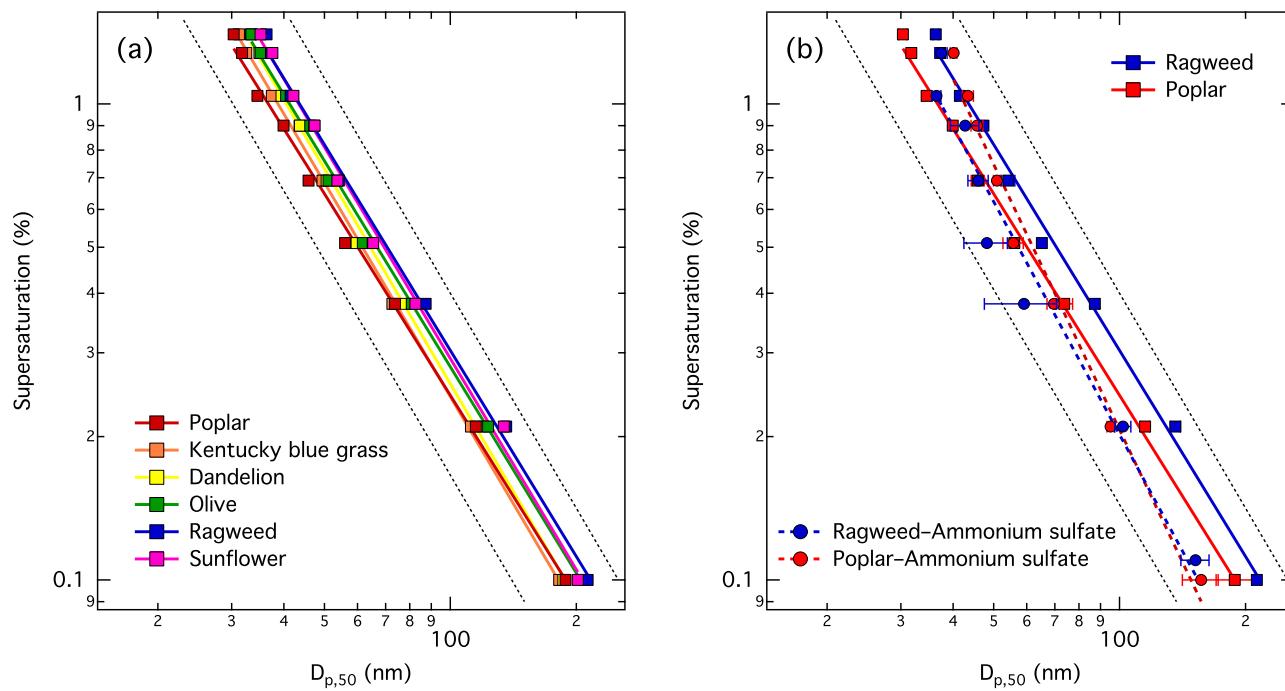
Figure 1. Measured CCN activity in terms of particle critical diameter ($D_{p,50}$) vs. supersaturation (SS) for particles comprising (a) six pure pollenkitts, and (b) mixtures of poplar and ragweed pollenkitt with 20% by mass of ammonium sulfate, shown together with results for the respective pure pollenkitt particles. Lines are fitted to the data to determine the slope in $\ln - \ln$ space. Dashed black lines have slope -3/2 in $\ln - \ln$ space and are on the graphs to guide the eye.

Table 3. Pollenkitt surface activity: Szyszkowski fitting parameters according to Equation 3 for aqueous solutions of ragweed and poplar pollenkitts and their mixtures with ammonium sulfate.

Sample	a [mN m^{-1}]	b [x10^{-4}g L^{-1}]	χ^2
Poplar	3.67±0.244	1.49±0.543	3.640
Ragweed	3.48±0.207	1.93±0.609	2.316
Poplar + 20 wt% AS	3.53±0.206	0.180±0.0623	3.530
Ragweed + 20 wt% AS	3.37±0.156	0.230±0.0615	1.841

pollenkitt average molecular masses using KTA to be 825–1130 and 400–550 g mol^{-1} for ragweed and poplar, respectively. For molecular masses in the range 100–1000 g mol^{-1}, the pollenkitt concentrations where surface tension drops below 50 mN m^{-1} correspond to 0.1–1 mM. The investigated concentration range covers those of stock solutions used for pollenkitt particle generation for CCN measurements. However, it is not possible to conclude that the critical micelle concentration for the

solutions is also covered by the investigated range, i.e. that the measured surface tensions have plateaued for the highest concentrations studied here.

We see that poplar pollenkitt is the stronger surfactant compared to ragweed, and in both cases that surface tension is decreased upon addition of ammonium sulfate compared to binary solutions with the same pollenkitt content. The latter ob-
5 servation indicates a modest salting out effect for the given PK:AS mixing ratio of 4:1 by weight, where ammonium sulfate increases pollenkitt aqueous activity and bulk-to-surface partitioning. Both observations suggest that surface activity might indeed affect pollenkitt CCN activity as well.
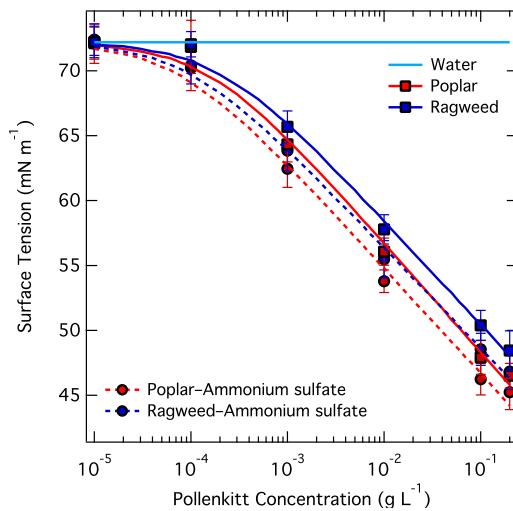
Figure 2. Measured surface tension of ragweed and poplar pollenkitts and their 20% by dry solute mass mixtures with ammonium sulfate, together with curves predicted by the ternary parameterization of Equation 3.

3.3 Pollenkitt experimental κ values

Measured CCN activity for the different pollenkitts and the mixtures of pollenkitt with ammonium sulfate were inverted ac-
10 cording to the relations given in Section 2.5 for obtaining κ values for each particle composition, size, and supersaturation state. Figure 3 show size resolved experimental κ values for pure dandelion, Kentucky bluegrass, olive, and sunflower pollenkitts in panels a)–d), and for pure poplar and ragweed pollenkitt, respectively, and their mixtures with ammonium sulfate, in panels e) and f). For each particle composition, average κ values for the measured supersaturation and particle critical size range and the standard deviation for this average is also shown. In general, the particle hygroscopicity is moderate to low, with κ values
15 for pure pollenkitts particles comparable to previous estimates of organic hygroscopicity from ambient measurements, which range from 0-0.25 (Shantz et al., 2008; Wang et al., 2008; Bougiatioti et al., 2009; Gunthe et al., 2009; Chang et al., 2010; Dusek et al., 2010; Cerully et al., 2011; Moore et al., 2012; Mei et al., 2013a, b; Cerully et al., 2015; Pöhlker et al., 2016;

Thalman et al., 2017). We find pollenkitt to be more hygroscopic than the whole pollen grains studied by Pope (2010) and Griffiths et al. (2012). This is consistent with pollenkitt contributing disproportionately to overall pollen hygroscopicity, but may also be related to varying hygroscopicity between different humidity regimes. In our measurements, the average κ values for pure pollenkitt particles follow the same order as CCN activity at 1 % supersaturation, ragweed $\approx$ sunflower $<$ olive $<$

5   dandelion $<$ Kentucky bluegrass $<$ poplar (see Table 2).

For ragweed pollenkitt, mixing with ammonium sulfate significantly increases particle hygroscopicity, as expected from the higher intrinsic hygroscopicity of the inorganic salt, $\kappa_{AS} = 0.61$ (Petters and Kreidenweis, 2007). This is however not the case for poplar, where overall particle hygroscopicity is observed to be both higher and lower in ammonium sulfate mixtures, compared to pure poplar pollenkitt, and the average κ value for mixtures is actually lower than for the pure pollenkitt. We

10   return to this point in the following sections.

It is immediately evident from Figure 3 that experimental κ values for all pure pollenkitts and the two mixtures with ammonium sulfate depend on particle size. As the measured activation curves are consistent across supersaturations, we believe that this size dependency is real rather than due to instrument artifacts. Furthermore, we note that the shape of the κ size dependency is similar for all particle compositions. In particular, for all pure pollenkitts, the κ values are stable at, or slightly below,

15   the respective average values, for particle sizes above roughly 70 nm. For smaller sizes, κ values first peak roughly between 50-70 nm, then steeply decrease, with possible further fluctuations, for still decreasing sizes. In several cases, the peak values are outside the rage of standard deviations for the average κ values.

We suggest that this size variation in particle hygroscopicity reflects the impact of pollenkitt surface activity on CCN activation. Since κ values are inverted under the assumption of constant pure water surface tension, any effect of surface tension

20   reduction on CCN activity is included in the resulting κ values. The relative diameter growth factor at the critical point of activation decreases with particle size (Prisle et al., 2010b), such that smaller particles activate as more concentrated solutions with higher surface area to bulk ratios compared to large particles. The size dependency in pollenkitt κ values thus reflects the changing relative contributions of surface partitioning and surface tension reduction. The smallest particles are depleted in bulk solute from bulk-to-surface partitioning, driven by the relatively large surface areas of small droplets. This effect is reducing κ

25   values to a greater extent than reduced surface tension from high droplet total concentrations simultaneously increases particle hygroscopicity. For somewhat larger particles, the relative magnitudes of these two competing effects are reversed. The surface partitioning of surface active pollenkitt is not longer strong enough to completely counter the increase in κ values from surface tension reduction. As particles get even larger, activating droplets become sufficiently large and dilute that nether of these effects are very strong, and the size dependency of κ values levels off.

30   For the pollenkitt–ammonium sulfate mixtures, the κ size dependency looks qualitatively similar to that generally observed for the pure pollenkitt particles. However, the peak κ value is shifted to smaller particles for ragweed and to larger particles for poplar compared to the pure pollenkitts. As mentioned above, κ values of ammonium sulfate mixtures with ragweed are higher than for the pure pollenkitt, while still lower than for pure ammonium sulfate, whereas κ values for poplar–ammonium sulfate mixtures are significantly lower than for pure pollenkitt at small particle sizes, with a strongly decreasing trend for decreasing size. Again, we believe that these observations reflect the impact of pollenkitt surface activity on CCN activation.
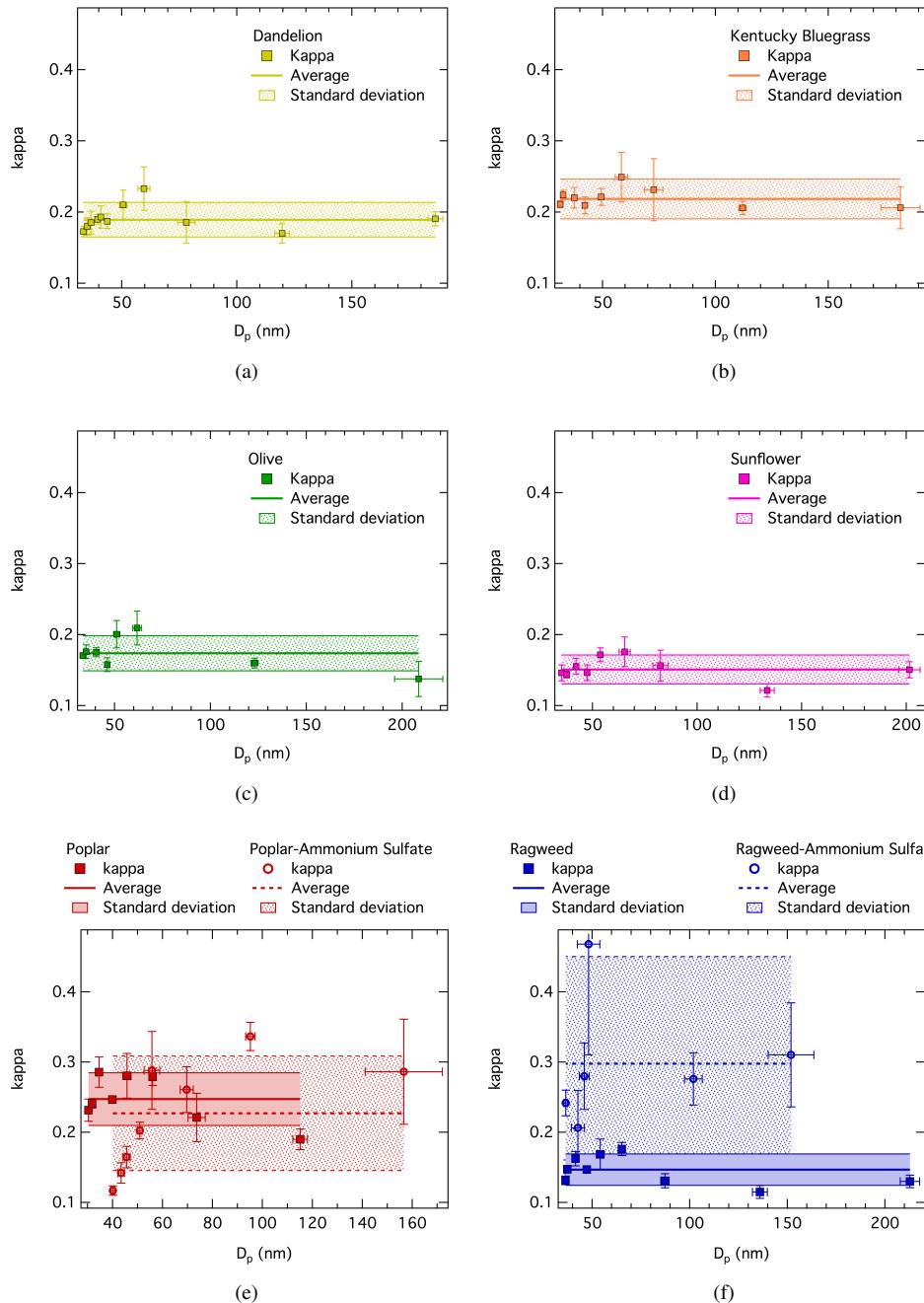
Figure 3. Hygroscopicity values κ from CCN activity measured by SMCA for all particle compositions. Panels (a)–(d) for pure dandelion, Kentucky bluegrass, olive, and sunflower pollenkitt. Panels (e) and (f) for pure poplar and ragweed pollenkitt, respectively, and their mixtures with ammonium sulfate.

As seen in Section 3.2, poplar pollenkitt is a stronger surfactant and, as we saw in Figures 1 and 3, has a greater intrinsic CCN activity (smaller critical size, large κ) than ragweed. For ragweed, we therefore see a stronger effect of salting out of pollenkitt by ammonium sulfate at the smallest and most concentrated activating droplets. First, κ values increase steeply with size, and as concentrations become more dilute, both surface activity and partitioning depletion effects quickly taper off. For poplar pollenkitt, these effects and their interaction are evident over a wider range of particle sizes and thus corresponding activating droplet concentrations, since effects of both bulk depletion from surface partitioning and surface tension reduction remain significant for more dilute droplet compositions.

3.4 Effects of surface activity on predicted pollenkitt CCN activation

Experimental particle CCN activity and derived κ values were compared to those obtained from different thermodynamic models, which account for effects of composition (assuming volume additivity) and surface activity (Prisle et al., 2010b, 2011), subject to different simplifying assumptions. The purpose is to test the applicability of these various models and their predictive strength for assessing hygroscopicity and cloud activation potential for the present case of complex atmospheric organic mixtures.

3.4.1 Thermodynamic Köhler models

Figure 4 shows predictions of CCN activity for pure and ammonium sulfate-mixed poplar and ragweed pollenkitt particles from the three thermodynamic Köhler models. In all cases, we have assumed a dry pollenkitt mass density of $1.2 \, \text{g cm}^{-3}$, which gave the best agreement with experimental CCN data over the density range $0.8 - 1.2 \, \text{g cm}^{-3}$.

Together with CCN activation, for each dry particle size and composition, we also evaluated the droplet surface tension specifically at the critical point of droplet activation. These results are shown in Figure 5 for the same model runs as shown in Figure 4. For both the pure pollenkitts, the full partitioning model typically predicts surface tensions in activating droplets which are about 10% reduced, compared to pure water. Model results are therefore shown here for the corresponding KTA-derived average effective molecular weights of $400 \, \text{g mol}^{-1}$ for poplar and $825 \, \text{g mol}^{-1}$ for ragweed pollenkitts, respectively, which are seen as the most internally consistent estimates. Over the range of KTA-derived pollenkitts molecular weights given in Section 3.2, corresponding to 0-10% reduction in droplet surface tension from pure water, all give essentially the same resulting CCN activity, reflecting the modest direct impact of molecular weight on modeled CCN activity for the two pollenkitts. This is also reflected in the similarity of CCN activity predicted with the full partitioning model and the water model omitting any effects of pollenkitt surface activity.

For mixed PK–AS particles, droplet surface tension at activation is typically slightly higher than for the corresponding pure pollenkitts. This reflects both that activating droplets are more dilute, due to the higher hygroscopicity of AS mixtures, as well as a small contribution from ammonium sulfate itself on aqueous surface tension.

Returning to Figure 4, we note that overall, neither of the three thermodynamic models is able to capture pollenkitt CCN activity well over the full particle size range studied. In particular, as observed in several previous studies for other atmospheric surfactants, the bulk model using droplet surface tensions based on total particle concentrations, and in particular omitting bulk
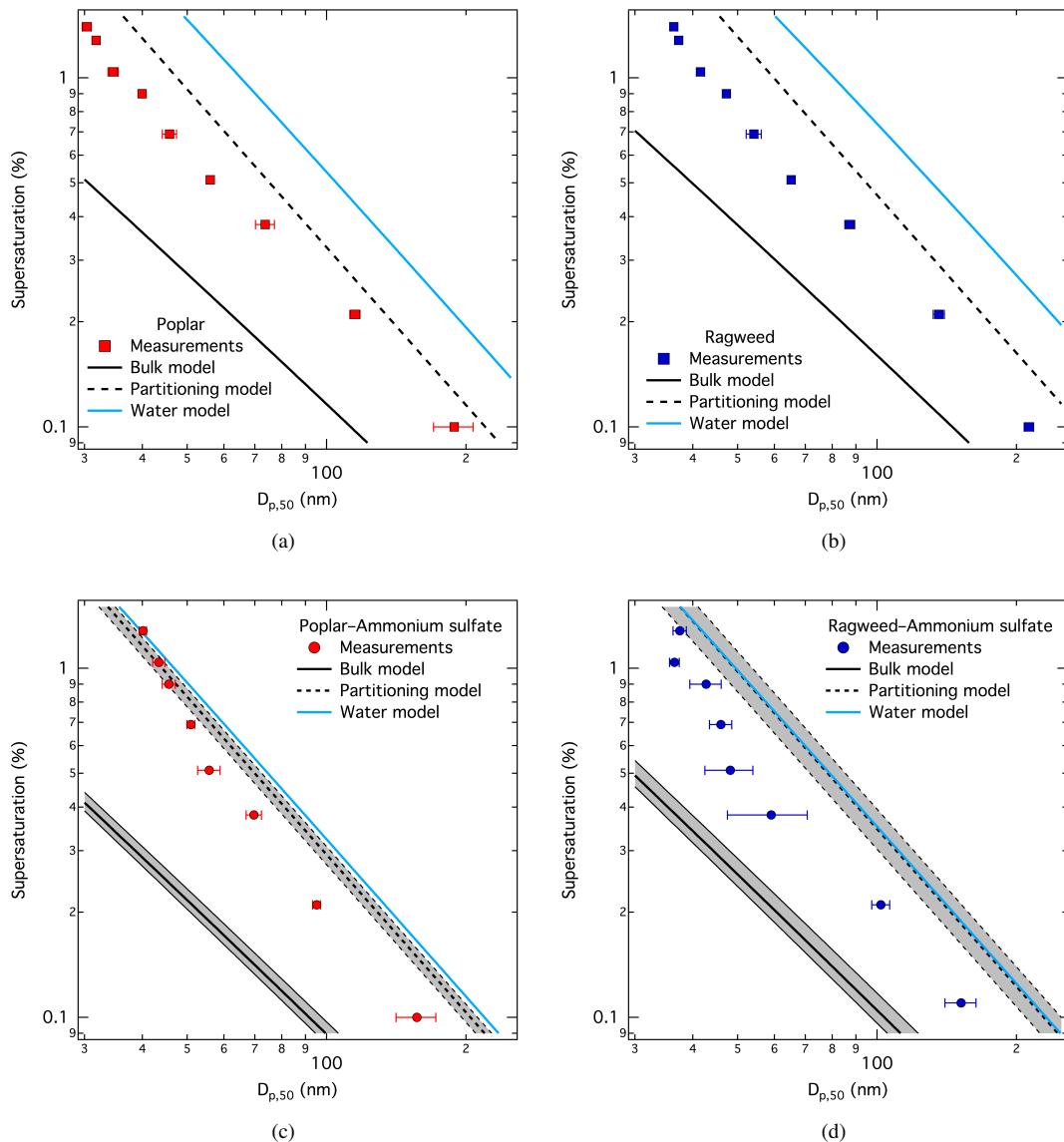
Figure 4. CCN activity modeled with the three different thermodynamic models (bulk, partitioning, and water) for particles comprising (a) pure poplar, (b) pure ragweed, (c) poplar and 20% by mass of ammonium sulfate, and (d) ragweed and 20% by mass of ammonium sulfate. For mixtures with ammonium sulfate, uncertainty ranges corresponding to a 10 wt% uncertainty in particle composition are indicated for the models including surface tension, bulk, and partitioning.
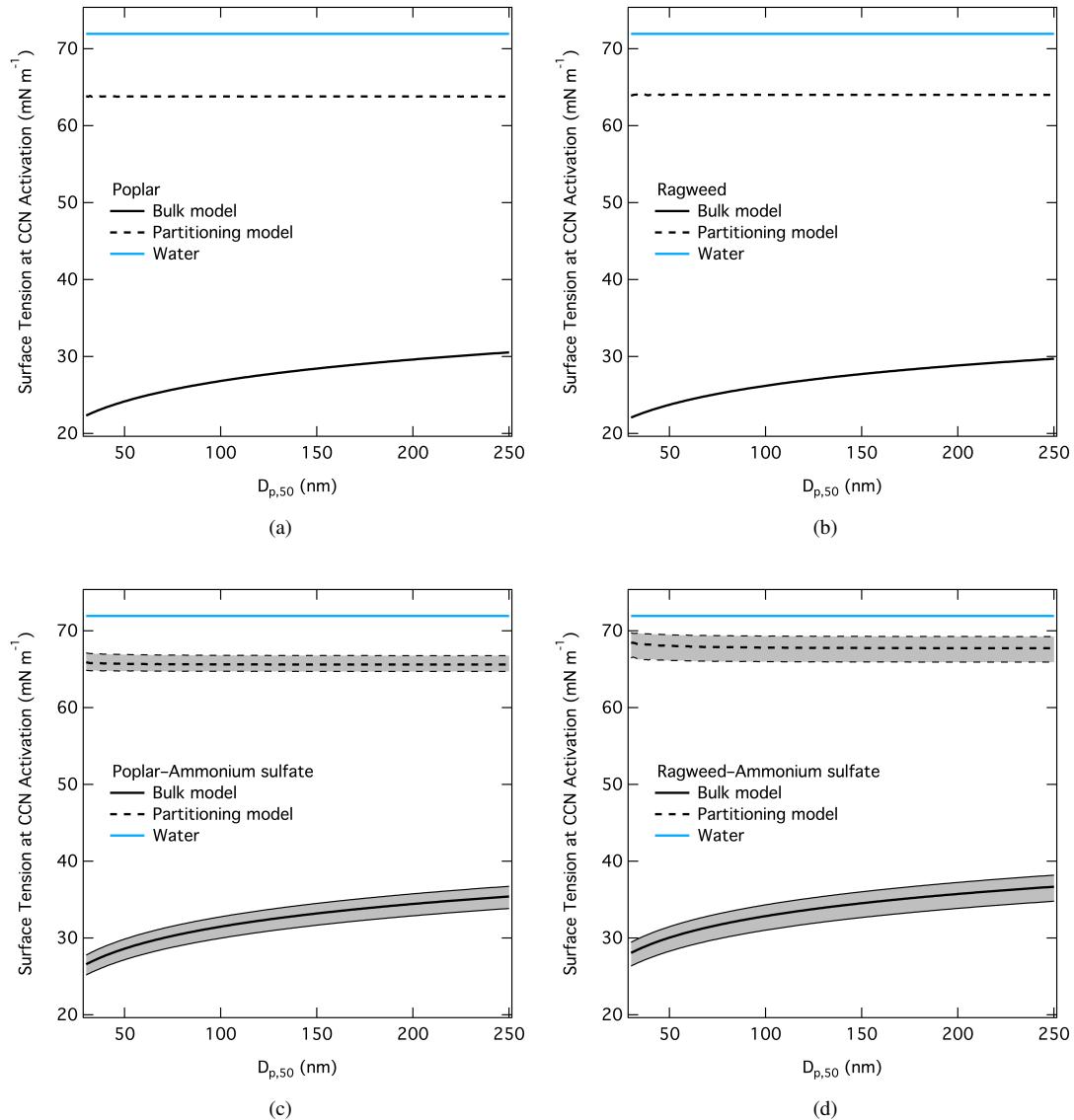
Figure 5. Droplet surface tension at the point of CCN activation modeled with the three different thermodynamic models (bulk, partitioning, and water) for particles comprising (a) pure poplar, (b) pure ragweed, (c) poplar and 20% by mass of ammonium sulfate, and (d) ragweed and 20% by mass of ammonium sulfate. For mixtures with ammonium sulfate, uncertainty ranges corresponding to a 10 wt% uncertainty in particle composition are indicated for the models including surface tension, bulk, and partitioning.

composition changes from surface partitioning, greatly overestimates measured CCN activity in all cases (Prisle et al., 2008, 2010b; Kristensen et al., 2014; Hansen et al., 2015). However, our most comprehensive and thermodynamically consistent partitioning model is also not able to predict pollenkitt CCN activity across the full investigated size range. In previous work, the partitioning model was observed to represent surface active organic aerosol CCN activity well, especially for 2-3 component model aerosol systems comprising relatively strong surfactants. Uncertainties in pollenkitt dry mass density and non-ideal aqueous activities, including unaccounted for synergy effects upon mixing with ammonium sulfate are likely contributing to this.

It has been suggested that laboratory-generated surfactant particles from nebulization of an aqueous stock solution can be enriched in surfactant, compared to non-surface active co-solutes like ammonium sulfate. In Figure 4, we show uncertainty ranges for mixed particle model results reflecting uncertainties in particle composition by a $\pm 10\%$ deviation in pollenkitt mass fraction. Even with such variations, we cannot reconcile any of the models with measured CCN activity. It is possible that the enrichment could be even more dramatic.

Both pollenkitts are seen in experiments to be more hygroscopic than predicted with the full partitioning model. The deviation is greater for pure pollenkitts and ragweed mixtures, compared to poplar mixtures, for which effects of bulk-to-surface partitioning are expected to be most pronounced as poplar pollenkitt is the strongest surfactant and mixing with ammonium sulfate is seen to lead to salting out. In general, measured CCN activity falls between predictions from the two models which include aqueous surface tension reduction from the pollenkitt. This suggests that surface tension indeed impacts CCN activity of the pollenkitt, but the overestimation of CCN activity by the bulk model also suggests that bulk depletion from surface partition plays a significant role as well.

The water model, which treats pollenkitt like a regular solute and neglects specific effects of surface activity, significantly underestimates CCN activity of the pure pollenkitts but gives similar results to the full partitioning model for the mixed particles. This suggests that surface activity indeed plays a role in determining CCN activity of poplar and ragweed pollenkitt and that the overall effect of surface activity is to enhance pollenkitt CCN activity. In pure pollenkitt particles, the effect of surface tension is therefore seen to be stronger than that of bulk depletion. As noted in previous work (Prisle et al., 2011), the water model may predict CCN activity well for strong surfactants, where bulk-to-surface partitioning plays a more significant role. However, other thermodynamic properties of activating droplets, such as bulk and surface composition and critical droplet size, may not be similarly well represented by the simplistic description. This may in turn have consequences for other aspects of atmospheric chemistry and aerosol-cloud-climate interactions (Prisle et al., 2012). Ruehl et al. (2016) recently experimentally verified these predicted differences in droplet size.

3.4.2 Simple partitioning

CCN activity predicted with the simple partitioning model are shown in Figure 6. The simple model only give meaningful results for mixed particles comprising a non-surface active hygroscopic components such as ammonium sulfate, because the hygroscopicity of surfactants is assumed to be vanishing. For the same reason, modeled results are identical for the two pollenkitts ragweed and poplar for a given assumed organic mass density regardless of the molecular mass of pollenkitt. In

5 Figure 6, we show results for three values of pollenkitt density over the range considered. We see that in all cases, the simple partitioning model strongly underestimates pollenkitt CCN activity, supporting the conclusion that droplet surface tension is indeed reduced at the point of CCN activation and also that pollenkitt has some intrinsic hygroscopicity, as further supported by the close similarity of predictions from both partitioning and water models. Perhaps counterintuitively, but as explained in detail in earlier work (Prisle et al., 2011), the simple representation work better for stronger surfactants. The pollenkitts

10 are fairly surface active, but evidently not enough to be well represented by the simple model which was developed for even stronger surfactants, like SDS and fatty acid salts with 10 or more carbon atoms.
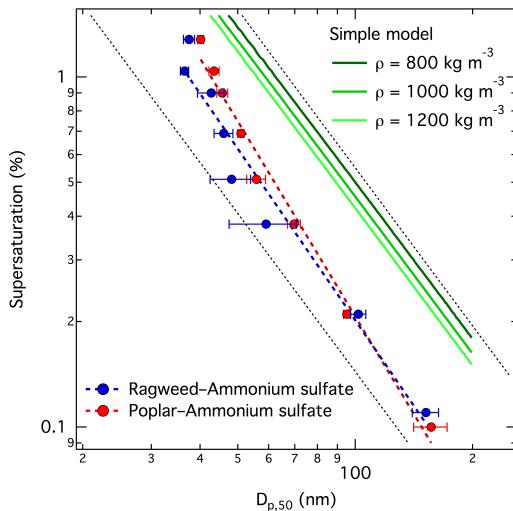
Figure 6. CCN activity modeled with the simple partitioning model for particles comprising pollenkitt and 20% by mass of ammonium sulfate. The simple model predicts the same CCN activation for all organics, given a specified dry organic mass density, as explained in the text. Model results are shown here for assumed pollenkitt densities of 0.8, 1.0, and 1.2 g cm^{-3} together with measured CCN activation for poplar and ragweed mixtures with ammonium sulfate. Dashed black lines have slope -3/2 in $\ln-\ln$ space and are on the graphs to guide the eye.

3.4.3 Modeled κ values

Experimental κ values for poplar and ragweed pollenkitts and their mixtures with ammonium sulfate are compared to those obtained from the three different thermodynamic models in Figure 7.

None of the models capture the shape of the size dependence of κ values. The partitioning model κ values hint of a very small decrease for the smallest particle sizes but not near the decrease observed in the experimental data. This observation is

5 believed to be caused by insufficient representation of the true ternary ammonium sulfate–pollenkitt aqueous phase interactions

using the pseudo-ternary surface tension parameterizations. These are based on a constant mixing ratio between ammonium sulfate and pollenkitt, whereas bulk-to-surface partitioning of the surfactant changes this ratio for the activating droplets. For highly pollenkitt-depleted smaller droplets, this ratio is significantly changed from the nominal 4:1 mixture. This aspect is discussed in more detail by Prisle et al. (2010b, 2011). One consequence is that the partitioning depletion for small droplets is likely to be strongly underestimated in our present model results.

κ values predicted with the bulk model increase steadily with decreasing critical particle size, reflecting how modeled surface tension of activating droplets decrease as these droplets get more concentrated. Bulk κ values are in all cases significantly greater than experimentally derived hygroscopicity. Interestingly, the predicted κ values for mixed particles are greater than for pure ammonium sulfate for both pollenkitts, reflecting that effects of surface tension in the absence of partitioning depletion of the droplets would lead to higher hygroscopicity of the organic than even a highly hygroscopic inorganic salt. For poplar, this effect is sufficiently pronounced to make even the intrinsic hygroscopicity of the pure pollenkitt particles larger than ammonium sulfate for the smaller particles, which activate as more concentrated droplets.

By design, the water model predicts constant κ values for particles under the ideal solution assumption applied here. Concentration-dependent water activity coefficients could potentially introduce a size dependency in κ values as droplets dilute. However, sensitivity studies in previous work have shown that this effect is likely very small for the water model, where droplets are in general relatively more dilute than for the partitioning model (Prisle et al., 2010b). The close similarity of mixed pollenkitt–ammonium sulfate particle κ values predicted with the partitioning and water models (for ragweed, these are essentially identical) underline the small overall effect of pollenkitt surface activity on particle activation. The opposing influences of surface tension reduction and partitioning depletion yield resulting κ values nearly identical to those predicted assuming no surface activity of pollenkitt. However, the difference between predictions for pure pollenkitt particles also indicate that this is partly due to the effect of the hygroscopicity of ammonium sulfate.

As we observed above, the strongest evidence for the presence of surface activity effects on CCN activation thermodynamics comes from the deviation of the slope of $\ln D_{p,50}$ vs. $\ln SS$ from the ideal solution value of -3/2, especially seen for the more surface active poplar mixtures with ammonium sulfate. From the experimental κ values, the size dependency in pollenkitt hygroscopicity is readily linked to surface activity through both surface tension and bulk-to-surface partitioning, as was also observed in previous work (Prisle et al., 2010b). Pollenkitt aqueous bulk solubility may play a role here as well. However, the major mechanism would result in overestimation of CCN activity by the water model as is only seen for the smallest poplar–ammonium sulfate particles, which are also the most concentrated at the point of activation.

4 Conclusions

Our measurements demonstrate that pollenkitt is moderately both hygroscopic and surface active. Considering in particular the size dependency of CCN activity and the hygroscopicity parameter κ, we see that surface activity indeed does impact pollenkitt cloud activation thermodynamics. Our most detailed model calculations show that surface tension of activating droplets is moderately reduced but not to the dramatic degree as has been suggested in studies of other biologically related
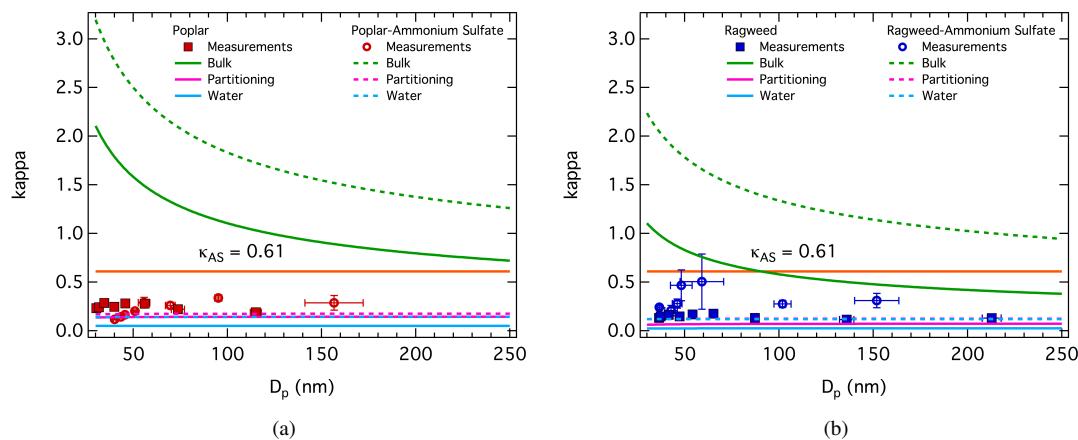
Figure 7. Hygroscopicity values κ derived from modeled CCN activity for (a) poplar and (b) ragweed pollenkitt particles and their mixtures with ammonium sulfate. Also shown are measured hygroscopicity values and κ value for pure ammonium sulfate for reference.

surfactants (e.g. Noziere et al., 2014; Ekström et al., 2010). The overall tendency is for surface activity to enhance pollenkitt hygroscopicity, in line with recent findings of Ruehl et al. (2016) for the hygroscopicity of secondary organic aerosol and Ovadnevaite et al. (2017) for primary organics in the marine environment. Contrary to our own previous work, which focused on stronger and/or chemically less complex surfactants, we here see evidence of both surface tension reduction in activating droplets, and a size dependency reflecting complex interactions between partitioning depletion (Raoult) effect and the surface tension effect (Kelvin) effect. Purely on its own, we find that pollenkitt tends to exhibit hygroscopic uptake properties that are similar to other complex organic systems, such as SOA that have a effective hygroscopicity somewhere between 0.1 and 0.2 (Andreae and Rosenfeld, 2008; Jimenez et al., 2009). This means that per unit mass of pollenkitt, the water uptake does not vary considerably between pollenkitts, so that the pollen uptake of water is driven primarily by the mass fraction of pollenkitt on the pollen particles - which is species-specific (Pacini and Hesse, 2005) - possibly in combination with pollen grain size or curvature of local features on the pollen grains.

We also find evidence for complex aqueous phase solute-solute interactions significantly impacting the size dependent hygroscopicity of pollenkitts and their mixtures with ammonium sulfate salt via bulk-to-surface partitioning and its enhancement from salting out. The immediate implication for pollen is that, depending on the species, the pollenkitt may have a considerably different response to condensation of sulfate, nitrate and other highly hygroscopic species. The response of pollen to atmospheric aging as a result of the different water uptake properties may therefore be much more diverse than expected from fresh pollenkitt. Apart from changes in the cloud forming potential of these particles, the different response in water uptake also has potentially profound implications for the adhesive and rupture characteristics of pollen.

5   These results add to an emerging picture of a role of surfactants in Köhler theory which is complex and far from fully resolved. Specifically, they also mean that understanding the pollenkitt-water interactions for pure and mixed pollenkitts may provide important insights for changes in allergenicity and biological function of pollenkitt in polluted and pristine environments.

Competing interests. The authors declare no competing interests.

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