

Is ammonium sulfate a good proxy for particle CCN activity during a biomass burning event?

Meagan Moore et al.[†]

Biomass burning is a significant source of gas and particle-phase ammonium and organic compounds in the atmosphere [1, 2]. The organic component of particles (20-80%)[3] presents a challenge for predicting particle hygroscopicity and subsequent cloud droplet formation due to the plethora of compounds with large ranges of solubility, reactivity, and surface tensions. Ammonium salts formed via acid-base reactions of ammonia with slightly soluble organic acids could potentially affect particle acidity, cloud condensation nuclei (CCN) activity, and hygroscopic growth of aerosols with a significant organic component [3, 4]. Experimental measurements showed an increase in particle-phase ammonium correlated to an increase in measured CCN activity of biomass burning aerosol (BBA) [5]. While there was also an abundance of particle-phase organic acids, real-time single particle measurements indicate that ammonium was chemically bound to sulfate, and not the organic acids [5]. A Köhler model was used to determine the necessary ammonium sulfate fraction of the particles required to reflect their observed CCN activity ($\kappa = 0.009-2.3$) for a specific ammonium event during the 2007 San Diego wildfires. Our results demonstrate that during this event, ammonium sulfate is not a good proxy for the BBA CCN activity. We anticipate that improved modeling of particle-phase ammonium and sulfate, in addition to other more hygroscopic organic compounds such as levoglucosan and organic acids frequently found in BBA, will help constrain cloud model predictions of biomass burning CCN activity.

INTRODUCTION

Biomass burning aerosol (BBA) is very abundant in the atmosphere. Due to the preferential removal by cloud activation of BBA, it is important to understand its interaction with water. Water uptake by aerosols is determined by their hygroscopicity, which is a factor strongly influenced by chemical composition. Interactions with water can in turn alter the aerosol's physical and chemical properties [6]. A higher hygroscopicity increases light scattering and enhances the ability for the aerosol to act as CCN. These processes are all essential for understanding the aerosol effect on the global radiation balance [7]. Water content can also affect the partitioning of semi-volatile species between the gas and particle phases, which affects aerosol composition [8] and aqueous chemistry [3].

Previous studies on BBA hygroscopicity have included both sub- and supersaturated conditions with growth factor (ratio of wet to dry diameter at a particular relative humidity) and CCN measurements. Using filter extractions of BBA from various biofuels, laboratory studies were done to compare aerosol water uptake with a hygroscopic tandem differential mobility analyzer (HTDMA) setup and a CCN counter [9]. The results show that the aqueous filter extractions are more hygroscopic than the organic fraction; however, the exact hygroscopicity also depended on the biofuel type itself [9]. The same result was observed during the Fire Lab at Missoula Experiment (FLAME) study, where the hygroscopicities were strongly dependent on fuel type [10].

To summarize the CCN hygroscopicity measurements, a single parameter for particle hygroscopicity, or kappa (κ) is used [11]. κ describes a

particle's water activity and typical values range from 1.4 (hygroscopic soluble salt) to about 0 (insoluble but wettable) for atmospherically relevant systems, therefore is strongly dependent on chemical composition [11]. Pure ammonium sulfate (AS) has a κ value of 0.6 [11]. In China, during a biomass-influenced event, a κ value of 0.2 was measured [12]; that of levoglucosan, a water-soluble sugar strongly associated with biomass burning. BBA lab studies have observed a range of κ from 0.06 for ponderosa pine to 0.7 for swamp sawgrass [10], while field measurements have noted a κ value of 0.01 for fresh soot-rich biomass and 0.55 for grass burning, with aged biomass ranging from 0.1 to 0.3 [7]. Extractions of filter measurements of BBA resulted in a κ of 0.064 for duff core in methanol and 0.252 of sagebrush in water [9]. Therefore, it appears that the BBA for the ammonium event during the 2007 San Diego wildfires ($\kappa = 0.009-2.3$) had a larger range than the previously observed values. During the 2007 San Diego wildfires, single-particle chemistry and CCN activity were measured [5]. In this paper, we used the measured CCN activity [5] to model the chemistry and determine if the BBA hygroscopicity is strongly dependent on the chemistry, as has been noted in previous measurements [7, 9, 10, 12].

EXPERIMENTAL: AMBIENT MEASUREMENTS

Ambient particles were sampled through a 1/4" stainless steel tube that extended through the exterior wall of the laboratory on the second floor of Urey Hall (32°52'31.66"N, 117°14'28.64"W) on the University of California, San Diego (UCSD) campus from Sunday, October 21 to Thursday, November 1, 2007. For this paper we are focusing only on one event during this period, from 12:00 AM

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PDT on October 25 to 12:00 AM PDT on October 27, 2007. Particle size distributions were measured concurrently by a scanning mobility particle sizer (SMPS, TSI Model 3936). CCN concentrations were measured in real-time with a streamwise thermal gradient CCN column [13], at a supersaturation (SS) of 0.29%, which is slightly higher than coastal clouds, but similar to highly convective clouds that are produced in areas of biomass burning. Total particle counts were measured with a condensation particle counter (CPC, TSI model 3007). The fraction of CCN active particles, or fCCN was obtained by taking the CCN/CPC ratio. Activation diameter was determined using fCCN and the cumulative SMPS size distribution; the size on the distribution at the corresponding cumulative fraction is the activation diameter. Real-time, single-particle measurements were obtained with an ultrafine aerosol time-of flight mass spectrometer (UF-ATOFMS)[14], which provided size and chemical composition of particles between 50-300 nm. Mass spectral marker $m/z +18$ was used for ammonium and $m/z - 97$ for sulfate. Further experimental and data analysis details are provided in [5].

EXPERIMENTAL: MODEL

Between 12:00 AM PDT on October 25 and 12:00 AM PDT on October 27, 2007 there was a strong increase in the single-particle ammonium signal during a strong increase in CCN/CN ratio (fCCN) from 0.2 to 0.5 [5]. Single-particle data showed that the ammonium was chemically bound with sulfate and not organic acids [5]. Using the approach of Petters and Kreidenweis [11], we modeled the fraction of AS that would be necessary to match observed CCN activity when mixed with fulvic acid, a proxy for organic biomass burning compounds. To determine the fraction of ammonium sulfate (fAS) that would be necessary to match the observed CCN activity, the hygroscopicity model [11] assumes the particles were either AS, fulvic acid or a homogenous internal mixture of these two compounds.

Equation (1) is used for the model and gives the critical supersaturation (S) needed for a particle with a given dry diameter (D_{dry}) and water activity (κ).

$$S(D) = \frac{D^3 - D_{dry}^3}{D^3 - D_{dry}^3(1 - \kappa)} \exp\left(\frac{A}{D}\right) \quad (1)$$

Where D is the diameter of the droplet, D_{dry} is the diameter of the dry particle (activation diameter), and A is a constant assuming a surface tension of pure water (0.072 J m^{-2}) and

298.15 K [11]. The overall value of κ follows a simple volume mixing rule,

$$\kappa = \sum_i \varepsilon_i \kappa_i \quad (2)$$

where ε is the volume fraction of each component. A particle consisting of a wettable yet insoluble compound with $\varepsilon = 0.95$ ($\kappa = 0.001$) mixed with $\varepsilon = 0.05$ fraction AS ($\kappa = 0.6$) yields an overall κ of 0.03095. The droplet diameter is determined from the solubility of the compound. Fixed inputs for the model are: (a) $\kappa = 0.6$ (ammonium sulfate), (b) $\kappa = 0.03$ (the 10 – 30 kDa fraction of fulvic acid), (c) the solubility of AS (infinite), and (d) the solubility of fulvic acid (unknown, approximated with that of adipic acid, 0.059 g/100 mL water). Variable inputs for the model are: (a) the activation diameter, and (b) ε of AS/fulvic acid. The input activation diameters are based on ambient measurements. Iterations were run on the model varying the ε of the two compounds until the critical supersaturation converged to that of the experimental CCN counter (SS = 0.29%). While we do not expect a surface tension of pure water for these particles, it is used to give us a relative comparison of the difference in particle chemistry and size observed. This approach is the best way to model our data, as we already know the activation diameter, the experimental supersaturation, and can vary the chemical mixing ratios of ammonium sulfate and fulvic acid to best match observations.

MODEL RESULTS

Figure 1 shows modeled overall κ , observed activation diameter, and modeled fAS. As the modeled overall κ increases, corresponding to increasing CCN activity and hygroscopicity, the observed activation diameter decreases, and the modeled fAS increases. Overall, modeled κ ranges from ~0.009 to 2.3 with a median value at approximately 0.04. Observed activation diameter ranges from 40 to 200 nm with a median value at approximately 190 nm. The inset graph shows the correlation between modeled fAS and the modeled overall kappa. This has a R^2 of 0.67, which is generally considered strong for ambient data. Overall, the modeled fAS is close to zero throughout the study, which is quite low. One notable event was around 12:00 PM PDT on October 25, 2007, where the modeled fAS spikes to almost 100% and then decreases back to nearly zero over five hours. At the peak of this spike (not shown), the fAS would need to be greater than 100% to account for the observed hygroscopicity.

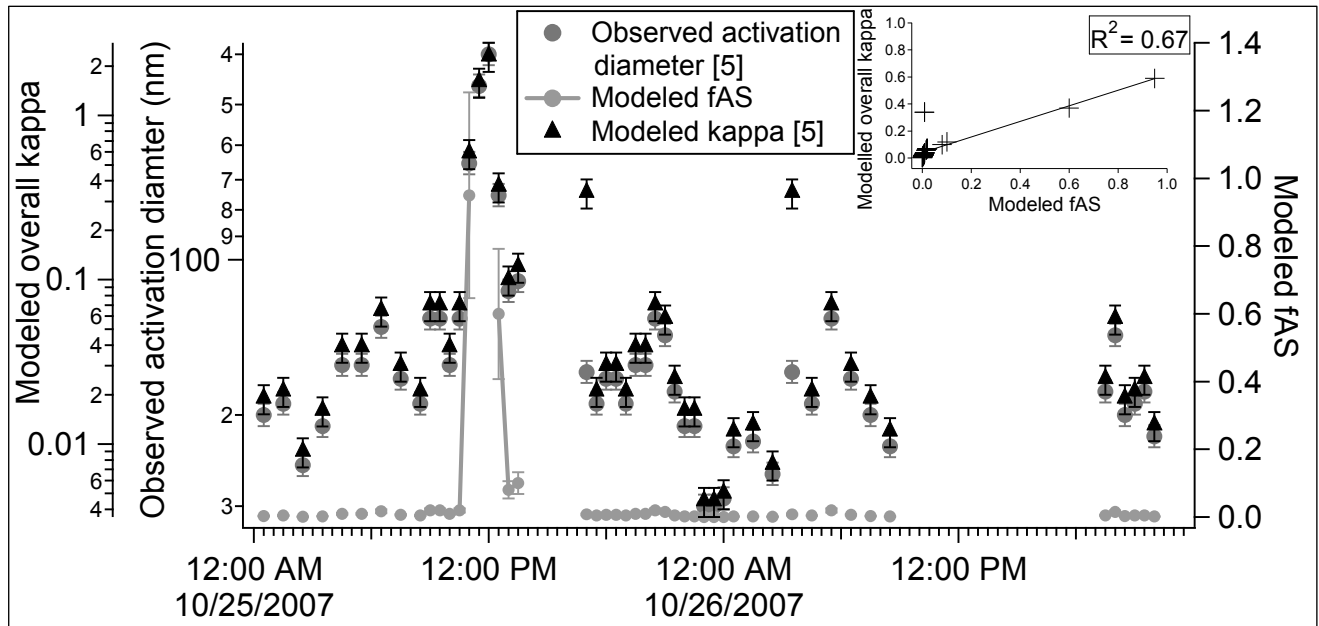


Figure 1. Modeled ammonium sulfate fraction (fAS) and hygroscopicity calculations with single hygroscopicity parameter κ . Also shown is observed activation diameter. Inset is a scatter plot of modeled observed kappa vs. modeled fAS. Dark gray circles are observed activation diameter, light gray circles are fAS and black triangles are modeled κ .

The observed κ during this time is 2.3, greater than the κ value of AS (0.6). A compound with a κ of this value is unknown and warrants further investigation, and could be a source of error for our predictions.

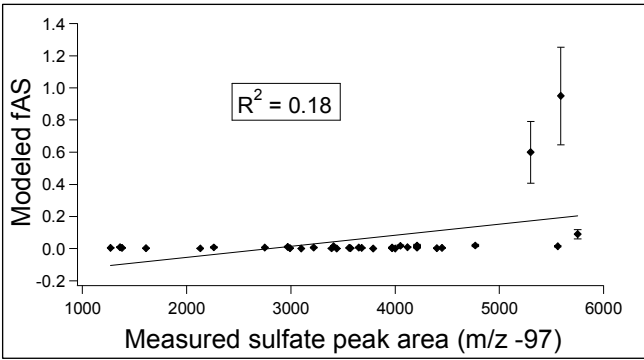


Figure 2. Modeled fAS compared to experimentally measured sulfate. Error bars are 30% uncertainty due to sizing uncertainty.

Figure 2 shows a direct comparison of modeled fAS (as previously shown in Figure 1) with observed single-particle sulfate [5]. The correlation between modeled fAS and measured sulfate is $R^2 = 0.18$. The uncertainty in fAS calculation from uncertainties in size, still does not account for disagreement between fAS and measured sulfate, as shown by the lack of overlap of the error bars (30% uncertainty) with the trend line on the scatter plot in Figure 2.

The model results show that AS alone is not a good proxy for BBA CCN activity during the ammonium event of the 2007 San Diego wildfires.

ROLE OF AMMONIUM SULFATE IN CCN ACTIVITY

Experimental measurements showed that fCCN was sensitive to the ammonium signal and this ammonium was primarily chemically bound with sulfate [5]. The hygroscopicity model of Petters and Kreidenweis [11] shows here that fCCN is not sensitive to the fAS modeled based on this CCN activity.

A known source of experimental uncertainty that contributed to the model is the uncertainty when combining the SMPS size distribution with fCCN to obtain the activation diameter. This uncertainty would need to take into account the experimental errors in sizing. There is a ~5% uncertainty in sizing from the SMPS which results in a ~20% uncertainty in κ and ~30% uncertainty in fAS. As shown in Figure 2, these uncertainties do not account for the disagreements between modeled and measured sulfate. Additionally, assuming constant composition with size is a large uncertainty, the quantification of which is beyond the scope of this model and paper.

When the model shows > 100% fAS needed, this is most likely due to the presence of a compound in the BBA that is more hygroscopic than AS ($\kappa > 0.6$) and/or the presence of organics. Surface-active organics could lower the surface tension and therefore increase the CCN activity. We chose AS and fulvic acid as the best proxies for the inorganic and organic fractions of BBA, respectively. However, it is significant that we observed a κ value > 0.6, as

it has been shown that BBA of swamp sawgrass has a κ value of 0.7 [10].

As AS alone is not a good proxy for biomass burning CCN activity, expanding the chemical inputs to the model to better represent BBA may help agreement between the model and the experimental observations. Additionally, the ammonium and sulfate were observed to both be mixed [5], however we were not able to determine (a) if they were indeed chemically bound and if so, (b) in what form; AS or ammonium bisulfate (ABS). If ammonium and sulfate are indeed present in the same particle, they are most likely in the form of AS or ABS, as this is the most thermodynamically stable form for ammonium. The aerosol pH can have profound effects on hygroscopic properties [4]. While the κ for ABS is currently unknown, the deliquescence relative humidity (DRH) for ABS is ~40% while the DRH of AS is ~80% [15]. Previous studies of BBA in the Amazon suggest that the majority of the inorganic component is actually ABS, not AS [16]. Therefore, these reasons alone could account for additional, yet unquantifiable, uncertainties in the model calculations of aerosol composition to CCN activity.

Our model assumes a fixed surface tension (constant A in Equation 1), of pure water. This is most likely not the case when organics such as surface-active fulvic acid are present in the particles [3]. Surface-active organics lower the surface tension and can make particles more CCN active. However, we chose a fixed surface tension because we wanted to compare relative changes in hygroscopicity assuming constant surface tension for all calculations. Varying the surface tension is something that should be addressed with future use of this model. Also, because we are not able to quantify the amount of organics on the particle, a small amount of surface-active organic may not affect the CCN activity significantly enough when in the presence of strongly hygroscopic compounds, such as AS. Previous studies on BBA and organics have noted that up to 80% of wet season aerosol mass is organic and that the sulfate could account for most of the CCN activity [16]. However, they also note that the CCN activity cannot be explained by the inorganic or organic composition alone, and that water-soluble and surface-active organic compounds could play a large role [16]. Due to the complexity of organic compounds found in atmospheric aerosol and the excessive fragmentation of organic compounds by our chemical composition measurement method, our observed change in fCCN was not correlated with any particle-phase organic markers [5].

CONCLUSION

During the 2007 San Diego wildfires, CCN activity was modeled with a hygroscopicity model. The model assumes that the biomass burning aerosol (BBA) is either ammonium sulfate (AS), fulvic acid or an internal mixture of the two compounds. The hygroscopicity model results are used and compared those to measured CCN [5]. The model results show that ammonium sulfate (AS) alone is not a good proxy for biomass burning CCN activity during the ammonium event of the 2007 San Diego wildfires. The calculated fraction of ammonium sulfate (fAS) does not correlate with measured sulfate. The ammonium and sulfate were observed to both be mixed [5], however we were not able to determine (a) if they were indeed chemically bound and if so, (b) in what form; ammonium sulfate or ammonium bisulfate. Additionally, uncertainty in size measurements (~5%) did contribute to large uncertainties in fAS calculations (~30%); however, these uncertainties do not account for the disagreements between modeled and measured sulfate.

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