

An annual cycle of size-resolved aerosol hygroscopicity at a forested site in Colorado

E. J. T. Levin,¹ A. J. Prenni,¹ M. D. Petters,² S. M. Kreidenweis,¹ R. C. Sullivan,¹ S. A. Atwood,¹ J. Ortega,³ P. J. DeMott,¹ and J. N. Smith^{3,4,5}

Received 12 September 2011; revised 11 January 2012; accepted 22 January 2012; published 16 March 2012.

[1] The ability of particles composed wholly or partially of biogenic secondary organic compounds to serve as cloud condensation nuclei (CCN) is a key characteristic that helps to define their roles in linking biogeochemical and water cycles. In this paper, we describe size-resolved (14–350 nm) CCN measurements from the Manitou Experimental Forest in Colorado, where particle compositions were expected to have a large biogenic component. These measurements were conducted for 1 year as part of the Bio-hydro-atmosphere Interactions of Energy, Aerosols, Carbon, H₂O, Organics, and Nitrogen program and determined the aerosol hygroscopicity parameter, κ , at five water supersaturations between $\sim 0.14\%$ and $\sim 0.97\%$. The average κ value over the entire study and all supersaturations was $\kappa_{\text{avg}} = 0.16 \pm 0.08$. Kappa values decreased slightly with increasing supersaturation, suggesting a change in aerosol composition with dry diameter. Furthermore, some seasonal variability was observed with increased CCN concentrations and activated particle number fraction, but slightly decreased hygroscopicity, during the summer. Small particle events, which may indicate new particle formation, were observed throughout the study period, especially in the summer, leading to increases in CCN concentration, followed by a gradual increase in the aerosol mode size. The condensing material appeared to be predominantly composed of organic compounds and led to a small decrease in κ at the larger activation diameters during and immediately after those events.

Citation: Levin, E. J. T., A. J. Prenni, M. D. Petters, S. M. Kreidenweis, R. C. Sullivan, S. A. Atwood, J. Ortega, P. J. DeMott, and J. N. Smith (2012), An annual cycle of size-resolved aerosol hygroscopicity at a forested site in Colorado, *J. Geophys. Res.*, 117, D06201, doi:10.1029/2011JD016854.

1. Introduction

[2] The biosphere, hydrosphere and atmosphere interact in complex ways through numerous linkages and feedbacks across a large range of spatial and temporal scales. Many of these linkages are understood, at least conceptually [Andreae *et al.*, 2002; Barth *et al.*, 2005; Kulmala *et al.*, 2004a]; however, much work remains to quantitatively understand these processes. The water and carbon cycles are particularly important in linking these systems. For example, soil moisture, relative humidity and precipitation all affect biological activity and emissions of biogenic volatile organic compounds [Barth *et al.*, 2005; Duhl *et al.*, 2008; Sharkey *et al.*, 2007; Telford *et al.*, 2010], while these biogenic emissions

can impact the number and characteristics of cloud droplet nucleating particles [Andreae and Rosenfeld, 2008; Fuzzi *et al.*, 2006]. Changes in cloud nucleating particles, in turn, can lead to enhancements in cloud reflectivity [Twomey, 1974], suppression of drizzle [Albrecht, 1989] and changes in intensity and distribution of precipitation [Rosenfeld *et al.*, 2008]. These changes in available water and sunlight complete the loop by further impacting the biosphere, although the strengths and directions of potential feedbacks are largely unknown.

[3] Biogenic secondary organic aerosol (BSOA) is a key component in this feedback loop. These particles form when volatile organic compounds emitted from vegetation are oxidized in the atmosphere forming lower vapor pressure reaction products which partition into the particle phase. Biogenic compounds can condense onto existing particles and are also an important contributor to new particle formation and growth events [Dusek *et al.*, 2010; Kulmala *et al.*, 2004a; Kulmala *et al.*, 2004b]. Organic particles compose a large fraction of the global submicron aerosol mass [Jimenez *et al.*, 2009; Zhang *et al.*, 2007], and biogenic precursors are a major source of these particles [Kanakidou *et al.*, 2005; Robinson *et al.*, 2011]. There are numerous species that contribute to this biogenic aerosol component, making it highly impractical to determine the cloud condensation

¹Department of Atmospheric Science, Colorado State University, Fort Collins, Colorado, USA.

²Marine Earth and Atmospheric Sciences, North Carolina State University, Raleigh, North Carolina, USA.

³Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado, USA.

⁴Department of Applied Physics, University of Eastern Finland, Kuopio, Finland.

⁵Kuopio Unit, Finnish Meteorological Institute, Kuopio, Finland.

nuclei (CCN) activity of these particles by considering the contribution of individual species to the overall hygroscopicity. Instead, laboratory studies [Asa-Awuku *et al.*, 2010; Engelhart *et al.*, 2011; King *et al.*, 2010; Massoli *et al.*, 2010; Petters *et al.*, 2009b; Prenni *et al.*, 2007] have been conducted to constrain the hygroscopic properties of model BSOA particles and link variations in these to precursor species and oxidation conditions. Field studies have also been conducted exploring ambient aerosol hygroscopicity in areas dominated by biogenic organic species such as tropical [Gunthe *et al.*, 2009] and boreal forests [Cerully *et al.*, 2011; Sihito *et al.*, 2010]. In addition, field studies have examined the seasonal variability in CCN concentrations and aerosol hygroscopicity [Fors *et al.*, 2011; Kammermann *et al.*, 2010] and the effects of organic dominated new particle formation on aerosol hygroscopicity [Dusek *et al.*, 2010].

[4] Here, we present yearlong measurements of size-resolved CCN activity from a forested location, providing additional data from a field-based location. In contrast to the tropical and boreal climates of the previous studies, we focus on aerosols inside a coniferous forest in a semiarid, midlatitude, continental location in Colorado. These measurements were conducted as part of the Bio-hydro-atmosphere Interactions of Energy, Aerosols, Carbon, H₂O, Organics, and Nitrogen (BEACHON) project, which seeks to better understand the interactions and feedbacks among the atmosphere, biosphere and hydrosphere through the carbon and water cycles. Measurements were conducted from spring 2010 through spring 2011, prior to the intensive BEACHON–Rocky Mountain Biogenic Aerosol Study (ROMBAS), which occurred in July and August 2011.

[5] A goal of the BEACHON project is to assess the impact of biogenic emissions of volatile organic gases and their oxidation products on the population of CCN. Because of the location of this study, we assume such impacts are primarily through the formation of BSOA which can modify CCN populations in one of three ways: by increasing total particle number concentrations through their participation in new particle formation; by shifting aerosol size distributions to larger sizes by condensing on existing particles; and by altering the hygroscopicity of particles onto which they condense. Although we do not have complete observations of BSOA precursors for the entire annual cycle covered in this study, Kim *et al.* [2010] recently reported PTR-MS observations of biogenic volatile organic compounds (BVOC) and their oxidation products from a 2008 intensive campaign at the BEACHON site. In addition, 2010 and 2011 measurements confirmed the presence of expected biogenic compounds, particularly, 2-methyl-3-butene-2-ol (MBO) and monoterpenes.

[6] Further evidence of biogenic impacts on the Rocky Mountain regional aerosol can be found in the work of Schichtel *et al.* [2008], who analyzed filters from the Inter-agency Monitoring of Protected Visual Environments (IMPROVE) network for ¹⁴C. Their objective was to develop a better understanding of the relative contributions of fossil (anthropogenic) and modern (largely biogenic) carbon to total carbonaceous aerosol. Total carbon aerosol includes both organic and elemental carbon, although as shown in their paper, the ratio of EC/TC at Rocky Mountain National

Park was on the order of 0.1–0.2. On the basis of their findings, in the Rocky Mountain region in which we were sampling, it is likely that over 90% of the total carbon aerosol was from contemporary sources during the summer. While anthropogenic sources increased in importance in the winter, contemporary sources were still dominant (>75% of the carbon aerosol). Thus, we expect biogenically derived organic carbon to be a major contributor year-round to the aerosol measured in our study, but with its relative contribution to aerosol mass concentrations increasing in the summertime.

2. Methods

2.1. Measurement Site

[7] The measurement site is situated in the Manitou Experimental Forest located in Pike National Forest, Colorado (38.64°N, 105.11°W). The site is at an elevation of 2300 m and is ~72 km southwest of Denver and ~40 km northwest of Colorado Springs. The Experimental Forest covers roughly 67 km² and is representative of the Central Rocky Mountains montane zone [Kim *et al.*, 2010]. In the vicinity of the measurement site, the vegetation is almost entirely open-canopy ponderosa pine. However, the Experimental Forest also contains large areas of Douglas fir, aspen and open grassy areas, and upwind ecosystems may include these species as well as oak and spruce forests, and riparian willow zones [Kim *et al.*, 2010]. The BEACHON site was specifically chosen to have minimal impact from nearby anthropogenic gas and particle emissions but to be in a region with significant BVOC emissions. The ambient submicron aerosol is expected to be dominated by organic compounds, primarily of biogenic origin.

[8] Back-trajectory residence time analysis using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model [Draxler and Hess, 1997, 1998; Draxler, 1999] and the Global Data Assimilation System (GDAS) 1° meteorological data set shows that air masses impacting the BEACHON site during the study period came predominantly from southwest Colorado (Figure 1), a sparsely populated mountainous region. Back-trajectories were rarely clearly impacted by air masses from the Front Range of Colorado, consistent with the findings from the prior study at this location by Kim *et al.* [2010]. While some seasonal variability exists (not shown), Southwest Colorado remained the dominant source region for air masses impacting our site in all seasons.

2.2. Instrumentation and Measurement Technique

[9] Our instrumentation was housed in a climate controlled, modified shipping container which was maintained at ~18°–20°C throughout the study. Sample was drawn at a rate of 1.5 LPM through an inlet which extended to ~3 m above ground level (AGL). Sample residence time in the inlet was approximately 6 s. After the completion of 1 year of sampling we also sampled for one month from an inlet ~25 m AGL. The tower to which this inlet was attached was located ~20 m from the container housing our instrumentation. For this higher inlet, air was drawn down through copper tubing (12.5 mm ID) by a 1/4 hp carbon-vane pump at ~10 LPM (resulting in a residence time of ~15 s) and our

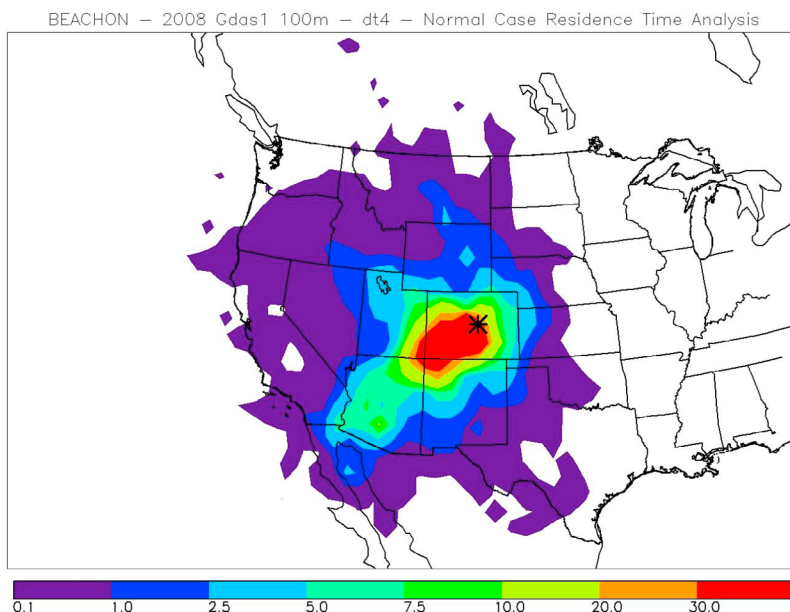


Figure 1. Annual residence time analysis for the Bio-hydro-atmosphere Interactions of Energy, Aerosols, Carbon, H₂O, Organics, and Nitrogen receptor site (asterisk) based on 2010 Hybrid Single-Particle Lagrangian Integrated Trajectory back-trajectories. Contours of 1° × 1° grid boxes indicate the relative average residence time of an air parcel in each grid box.

sample flow was then drawn off of this larger flow immediately ahead of the instrumentation. We made no corrections to the aerosol data for particle losses in the inlets.

[10] Total aerosol and CCN size distributions were measured using a condensation particle counter (CPC; model 3010 or 3760, TSI Incorporated, Minneapolis, MN) and a cloud condensation nucleus counter (CCNC; Droplet Measurement Technologies, Boulder, CO) downstream of a differential mobility analyzer (DMA; TSI 3071) following the setup described by *Petters et al.* [2007, 2009a]. The DMA had a sheath to sample flow ratio of 10:1.5. After being drawn into the container, sample flow first passed through a diffusion drier and a bipolar charge neutralizer (Aerosol Dynamics Inc.), containing four ²¹⁰Po strips (NRD Static-master 2U500). The charging strips were replaced twice during the study so the strips were never older than 6 months. Particles were then size selected using the DMA and the quasimonodisperse sample flow was split and sent to the CPC (1 LPM) and CCNC. The CCNC had a total flow of 0.5 LPM with a sheath to sample flow rate ratio of 10:1. The DMA stepped through 20 different dry particle diameter settings between 14 and 350 nm and measurements were made at each size for 30 s. The DMA midpoint diameters were chosen such that $\text{dlog}_{10}D_p$ was approximately constant. After stepping through all sizes, the CCNC supersaturation was changed and the DMA size steps were repeated. Supersaturation ($s = \text{RH} - 100\%$) inside the CCNC is controlled by the temperature gradient (ΔT) along the flow column with larger ΔT values resulting in higher s [*Roberts and Nenes, 2005*]. Five different ΔT settings were used for this study: 4°, 8°, 12°, 16°, and 19°C. A full cycle, stepping through all 20 DMA size bins at each of the 5 CCNC ΔT settings, took about 75 min after which there was a five minute delay to allow the CCNC column to return to the lowest ΔT setting.

All DMA and CCNC settings were controlled automatically by a LabVIEW program (National Instruments, Austin, TX).

[11] The s inside the CCNC flow column was determined for each ΔT setting by calibrations performed with ammonium sulfate aerosol generated using a TSI 3076 atomizer [*Petters et al., 2009a; Rose et al., 2008*]. For each calibration scan, data from the CCNC and CPC were used to generate CCN activation curves (the fraction of particles that activate as CCN at the set point s as a function of dry particle diameter). The activated fraction was fit with a Gaussian cumulative distribution function weighted by the Poisson counting statistics in each size bin, and the midpoint of these curves, the diameter corresponding to 50% activation, was taken as the critical activation diameter (D_c). The critical supersaturation (s_c), the supersaturation at which the particle activates into a droplet, corresponding to this dry diameter was then determined using Köhler theory and the thermodynamic properties of ammonium sulfate aqueous solutions as prescribed by the Aerosol Inorganics Model [*Clegg and Brimblecombe, 1998*]. Calibrations were performed automatically at each of the five CCNC ΔT settings slightly less than once per day (time between repeat calibrations at the same ΔT was about 27 h). All CCN data were interpreted using the most recent calibration point at the same ΔT setting. Table 1 shows the average and one standard deviation s value for each ΔT setting for the entire study as well as the associated range in κ calculated from the standard deviation in s . Table 1 also lists D_c values for a particle with a hygroscopicity parameter, κ [*Petters and Kreidenweis, 2007*], of 0.2 at the average s values.

[12] Because of differences between ambient and trailer temperature, as well as heating inside the CCNC column, some volatile organic species may have been lost, thus introducing a bias into our measurements [*Asa-Awuku et al., 2009*;

Table 1. Study Average Supersaturation (s) Values Determined From Ammonium Sulfate Calibrations at Each CCNC ΔT Setting and Corresponding Critical Activation Diameters (D_c) for a Particle With $\kappa = 0.2$ as Well as the Range of κ From the Range in s at the D_c in the Third Column^a

ΔT ($^{\circ}\text{C}$)	s (%)	D_c ($\kappa = 0.2$) (nm)	\pm in κ (from \pm in s)
4	0.14 ± 0.01	152 ± 14	0.06
8	0.36 ± 0.01	81 ± 3	0.02
12	0.56 ± 0.01	60 ± 2	0.01
16	0.78 ± 0.06	47 ± 5	0.07
19	0.97 ± 0.06	42 ± 3	0.05

^aSymbol \pm indicates 1 standard deviation.

Poulain et al., 2010]. Any loss of organic material, which has generally low hygroscopicity, would enhance the importance of more hygroscopic species such as ammonium sulfate in the aerosol. Thus, a decrease of the organic fraction should manifest itself in an inverse correlation of κ with ambient temperature. We observed no such correlation; however, because the trailer temperature remained roughly constant, we cannot fully test this hypothesis. Further studies, using an experimental configuration specifically designed to look for such effects, are needed in order to better understand the role of volatilization in influencing CCN measurements of ambient aerosol.

[13] There were no significant instrument problems with the CCNC throughout the yearlong study period. There were, however, several failures of the CPC, and several different CPCs were used during the study. A TSI 3010 was used from 12 March to 6 June, a TSI 3760 from 10 to 18 June, a different TSI 3010 from 24 June to 8 July, and finally a third TSI 3010 from 8 July through the end of the study. When changing CPCs, no changes were observed in measured aerosol concentration due to differences in CPC counting efficiency.

2.3. Hygroscopicity Parameter κ

[14] We use the hygroscopicity parameter, κ , presented by *Petters and Kreidenweis* [2007] to describe the hygroscopicity of the aerosol measured during this study. Köhler theory, which defines the saturation ratio, S , over a droplet can be written in terms of κ , as follows:

$$S(D) = \frac{D^3 - D_d^3}{D^3 - D_d^3(1 - \kappa)} \exp\left(\frac{4\sigma_{s/a}M_w}{RT\rho_w D}\right), \quad (1)$$

where D and D_d are wet diameter and dry diameter, $\sigma_{s/a}$ is surface tension of the air-water interface, assumed to be equal to the surface tension of water, $\sigma_w = 0.072 \text{ J m}^{-2}$, R is the universal gas constant, T is temperature and M_w and ρ_w are the molecular weight and density of water. The maximum of equation (1) is the critical saturation ratio, S_c , from which we can calculate critical supersaturation ($s_c = (S_c - 1) \times 100$).

[15] We followed the procedure presented by *Petters et al.* [2009a] to calculate κ values from our data. First, both the number distributions measured by the CCNC and CPC were corrected for multiply charged particles. Because we only measured up to 350 nm and did not use an impactor on the DMA inlet, there could be some unconstrained contribution from multiply charged particles with diameters larger than

the upper end of our measured distribution. However, at our s values we are concerned with particles with critical activation diameters of 150 nm and smaller (see Table 1). At the DMA flow settings used here, a particle larger than 350 nm would need to carry an electrical charge of four to have sufficient mobility to be sized smaller than 150 nm. However, it should be noted that for particles larger than ~ 350 nm, the fraction of singly charged particles decreases while the fraction of multiply charged particles increases. Thus, it is possible that the particles sent to and activated in the CCNC, particularly at the lowest supersaturation, may reflect the composition and hygroscopic properties of particles larger than 350 nm.

[16] After inverting the CPC and CCNC data we constructed CCN activation curves and found critical activation diameters as described above for the ammonium sulfate calibrations. The curve fitting routine not only returned the 50% activation diameter, assumed to be the critical activation diameter, but also the uncertainty in this parameter weighted by the Poisson counting statistics. The critical activation diameter for each scan was then used along with the s inside the CCNC to determine κ using equation (1) as follows. For a specified κ and D_d , wet diameter was varied iteratively until we found the maximum, i.e., the critical supersaturation, of equation (1). This process was repeated for a 2D matrix of geometrically spaced D_d and κ values to construct a lookup table that relates s_c , D_d , and κ . κ was then found from a set of measured D_d and s_c by performing a four point nearest neighbor interpolation found in the lookup table.

3. Results and Discussion

3.1. Kappa

[17] Figure 2 shows daily averaged κ values determined at the five CCNC s settings for the entire study period. Gray lines show daily standard deviation (note that this is showing the daily variability in κ , not the Poisson-counting uncertainty in κ discussed in section 2.3, which is shown in Figure 3, discussed below). Breaks in the timeline are due to the instrument malfunctions mentioned above. Figure 2 also shows the corresponding changes in critical activation diameter at each s setting. Daily averaged κ for sub-100 nm particles ($s = 0.36\%–0.97\%$) showed only small seasonal changes with values remaining ~ 0.15 for much of the study. To place these results in context, typical values of κ determined from laboratory measurements are 0.5–1.4 for hygroscopic salts such as ammonium sulfate and ammonium nitrate, ~ 0.1 for fresh secondary organic aerosol and ~ 0 for nonhygroscopic, wettable components [*Petters and Kreidenweis*, 2007; *Prenni et al.*, 2007]. Studies have also been performed to determine κ values of ambient aerosol in locations dominated by BSOA. For example, *Gunthe et al.* [2009] report an average κ value of 0.15 for measurements during the organic-aerosol-dominated wet season in the Amazon rain forest, while *Sihto et al.* [2010] and *Cerully et al.* [2011] found average κ values of 0.18 and 0.20 at a forested boreal site in Hyttiälä, Finland, respectively.

[18] While there was little change in κ values at the higher s settings, at $s = 0.14\%$ there was a noticeable decrease in daily averaged κ during the summer. Since κ is tied to the chemistry of the aerosol, this indicates some shift in chemical composition in the particles that activated at the lowest s

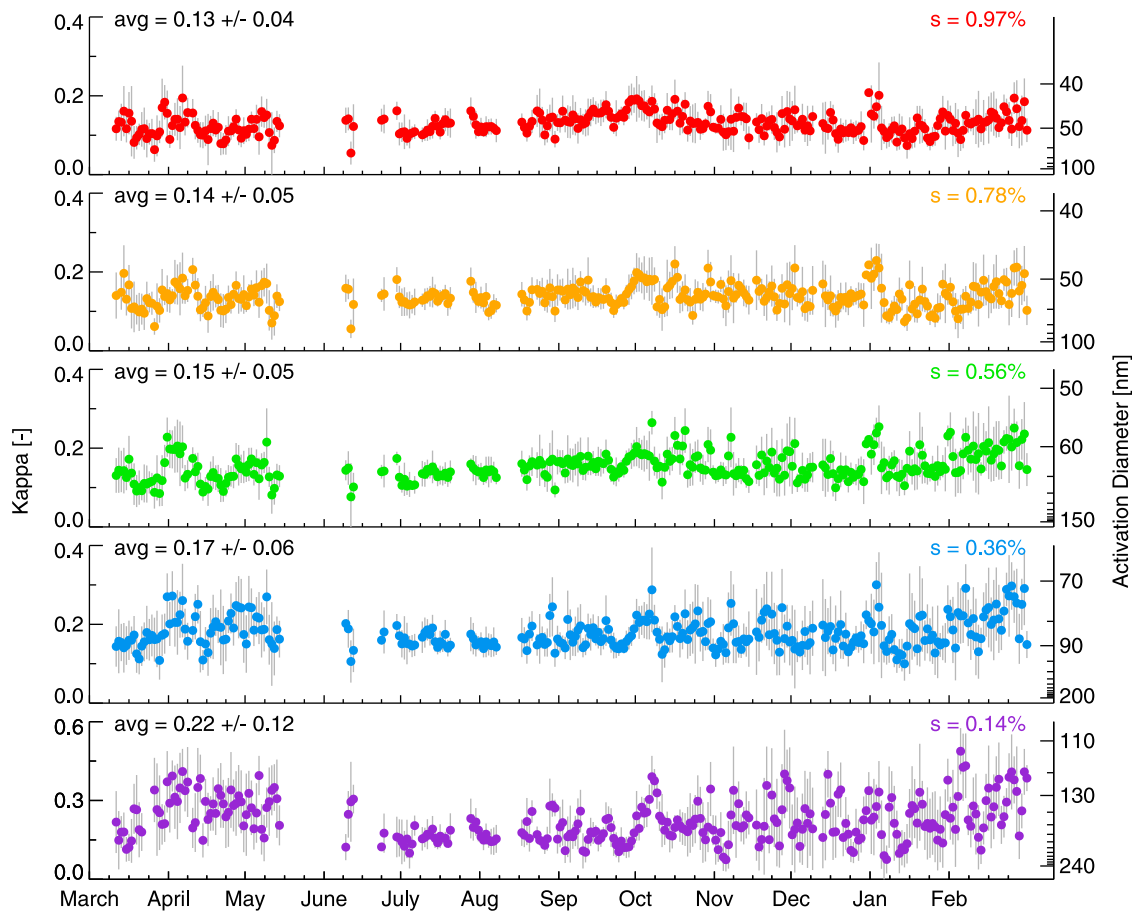


Figure 2. Daily averaged κ values at each supersaturation setting for the entire study period. Bars indicate daily standard deviation in κ . Right axis indicates the corresponding change in critical activation diameter (minor ticks are spaced every 10 nm).

setting, i.e., particles with diameters of ~ 150 nm and larger. During the summer there was also much less variability in κ for the $s = 0.14\%$ measurements than during the other seasons. Much of the higher variability in κ is due to the low CCN number concentrations during the winter months, especially at the lower s settings where fewer particles activate as CCN. However, even with this large variability, the

decrease in κ at $s = 0.14\%$ from spring to summer, and the subsequent increase in κ in the fall, was statistically significant at the 99% confidence level using a two-tailed t test.

[19] Study average (± 1 standard deviation) κ values, determined at each s setting, are also given in Figure 2. At higher s we observed κ values similar to those determined in laboratory SOA studies [e.g., *Prenni et al., 2007; Duplissy et al., 2008;*

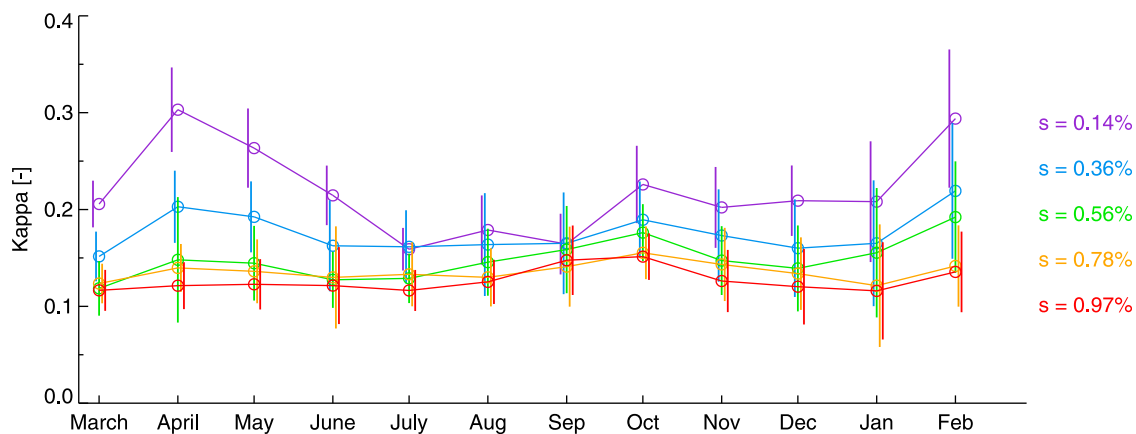


Figure 3. Monthly averaged κ at the five supersaturation settings. Bars represent monthly averaged uncertainty in κ from curve fitting.

King *et al.*, 2010]. There was a slight increase in average κ with decreasing s , from 0.13 ± 0.04 at $s = 0.97\%$ to 0.22 ± 0.12 at $s = 0.14\%$. These means are statistically different, with 99% confidence intervals, determined using the t statistic, of ± 0.002 and 0.004 , respectively. This shift in κ indicates a size-dependent chemical composition with the largest particles, characterized in the $s = 0.14\%$ scans, having slightly higher hygroscopicity. This increased hygroscopicity of the largest particles may be due to the fact that larger particles are likely more aged and may have been cloud processed, and thus may have a larger inorganic component [Fors *et al.*, 2011].

[20] Seasonal differences in κ as a function of s become more apparent when examining monthly averaged κ values (Figure 3). Lines in Figure 3 show the monthly averaged uncertainty in κ calculated from the uncertainty in activation diameter reported by the curve fitting routine. During July–September, there was essentially no difference in κ at the different CCNC measurement settings. For example, during the month of September the range in κ from the lowest to highest s setting was only 0.16–0.15, with uncertainties in κ of ~ 0.03 at both settings. The range in κ increased later in the fall and winter months and had a maximum during the spring ($\Delta\kappa = 0.18$ in April). These differences in April monthly averaged κ values at the highest and lowest s are statistically significant at the 99% confidence level using a two tailed t test. At $s = 0.14\%$, κ showed the largest seasonal variability with a peak value of 0.3 in April, steadily decreasing to a minimum value of 0.16 in July and September, and then increasing back to 0.3 in February. Kappa at higher s showed some similar features; however, there was decreased seasonal variability with increasing supersaturation. The seasonal changes in κ indicate that, on average, the aerosol population during the summer months was less hygroscopic than in the spring and fall, especially at the larger diameters. This observation would be consistent with an increase in aerosol organic fraction during this time period, as organic species are less hygroscopic than soluble inorganic salts. However, we note that other aerosol constituents, such as black carbon and dust species, also have a low hygroscopicity and increases in their relative contributions to the sub-micron aerosol mass concentrations can also reduce the observed κ .

3.2. Kappa and Aerosol Composition

[21] Kappa is a function of aerosol chemical composition and the κ values for many individual compounds, both inorganic salts and secondary organic species, have been determined from laboratory studies. Thus, while we have no aerosol composition data from this study, we can use κ values as an indicator of bulk aerosol composition.

[22] Petters and Kreidenweis [2007] showed that the κ of a mixture follows a simple mixing rule:

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

where ε_i and κ_i are the volume fraction and κ of each individual component in the aerosol. This mixing rule has been shown to apply to mixed organic and sulfate particles [King *et al.*, 2007; King *et al.*, 2010]. Gunthe *et al.* [2009] used this approach in reverse to calculate κ based on measurements

of aerosol composition from an Aerosol Mass Spectrometer (Aerodyne Research Inc., Billerica, MA) in the Amazon rain forest. They found good agreement between κ calculated from this two component (organic plus sulfate) composition assumption and that calculated from size-resolved CCN measurements, with submicron organic mass fractions of 0.65–0.95 during the Amazonian wet season.

[23] We follow this same approach with our data, assuming a two component aerosol containing organic species ($\kappa_{\text{organic}} = 0.1$) and inorganic salts ($\kappa_{\text{inorganic}} = 0.6$, for predominantly sulfate aerosol). Sulfate aerosol from anthropogenic sources has been shown to be present year-round in the Rocky Mountain area [Levin *et al.*, 2009; Malm *et al.*, 1994, 2004], likely as a component of the regional background aerosol. Along with organic aerosol, these species generally represent the dominant mass fractions of the PM_{2.5} aerosol in the region [Levin *et al.*, 2009].

[24] Our low κ values indicate that organic species dominate the aerosol in Manitou Forest throughout the year. The slightly higher, and more variable, κ values at larger sizes (lower s) indicate some size- and season-dependent changes in aerosol hygroscopicity; still, average κ values indicate that organic mass fraction (X_{organic}) was ~ 0.8 or greater for sub-350 nm aerosol throughout the study. While there is some uncertainty in the value assumed for κ_{organic} [Petters *et al.*, 2009b], the range in this value is low, generally $0.05 < \kappa_{\text{organic}} < 0.2$. Thus, even if the organic aerosol makeup varies considerably over the year, changes in measured κ would be small for organic dominated aerosol, consistent with our observations. Even for the extreme case of $\kappa_{\text{organic}} = 0$, our monthly averaged κ values indicate that organic species were still the dominant component with $X_{\text{organic}} > 0.5$ for all diameters and > 0.75 for the sub-100 nm aerosol (determined from $s > 0.14\%$ measurements).

3.3. CCN Variability

[25] In addition to changes in aerosol hygroscopicity during the study, there were also large changes in CCN number concentration. Figure 4 shows monthly averaged CCN number concentrations as well as the total aerosol number concentration ($D_p = 14\text{--}350$ nm) determined from CPC measurements. Total aerosol concentrations were highest in July and dropped to their lowest value in December. We observed a similar seasonal variability in aerosol volume concentrations estimated from our measurements (Figure 5). The January median value was $0.31 \mu\text{m}^3 \text{cm}^{-3}$, whereas the July value was $1.6 \mu\text{m}^3 \text{cm}^{-3}$. For reasonable aerosol densities in the range $1\text{--}2 \text{g cm}^{-3}$, these estimates of seasonal variations in total submicron mass concentrations are consistent with those in the limited data set of Schichtel *et al.* [2008], who reported aerosol carbon-only concentrations in the Rocky Mountain region of $\sim 2 \mu\text{g m}^{-3}$ during the summer, and $\sim 0.5 \mu\text{g m}^{-3}$ during the winter. Note that these values must be multiplied by an appropriate factor to account for the molecular form of C (~ 1.8 if organic dominated, ~ 1 for elemental carbon).

[26] Concentrations of CCN followed a similar trend and were 3 times higher in July than December for all but the $s = 0.14$ measurements, for which they were roughly double. The monthly averaged activated fraction (the fraction of total particle number concentration measured by the CPC that activated as CCN) showed a slightly different trend than that

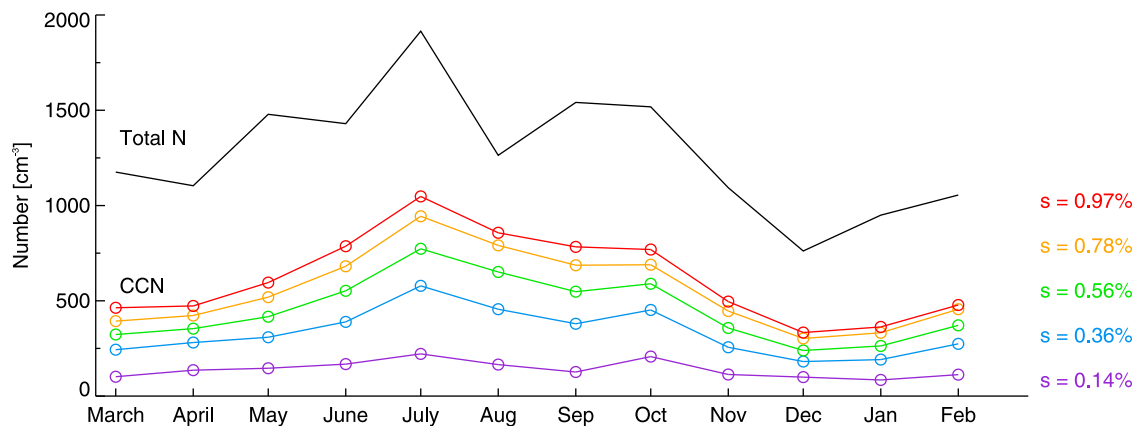


Figure 4. Monthly averaged total aerosol, $14 < D_p < 350$ nm (black), and CCN (colored) concentrations.

of CCN concentration (Figure 6). Instead of peaking in July, the maximum activated fraction (again excluding $s = 0.14\%$ measurements) occurred in August, with a value of 0.68 at $s = 0.97\%$. At the $s = 0.14\%$ setting, activated fraction showed essentially no seasonal change, remaining around 0.1 for the entire study. Since we were only measuring the sub-350 nm aerosol, we may have missed the contributions of larger particles to the total number concentrations. However, even in the presence of an event having a large-diameter mode (e.g., a dust event), the contributions to the total number concentrations at a particular s are expected to be negligible, except perhaps for the $s = 0.14\%$ mode.

[27] Number concentrations of CCN should be strongly correlated with total aerosol number concentrations if κ and size distribution remain the same. However, given that average κ values were lower in summer, it might seem surprising that there is a maximum in the fraction of particles that activate as CCN during this time. This apparent discrepancy can be reconciled by examining the changes in aerosol size distribution during the study. Figure 7 shows the monthly averaged geometric mean diameter (D_{gn}) and geometric standard deviation (σ_{gn}) for the aerosol number distributions. There was a clear increase in D_{gn} during the summer, peaking in August. Since CCN activation is a function of both hygroscopicity and particle size, this increase in D_{gn} was sufficient to increase the activated

fraction to a maximum during the summer, even with the decrease in κ .

3.4. Small Particle Events

[28] Throughout the study, we observed numerous examples of increases in number concentrations of the smallest measured particles, with subsequent evolution of the aerosol size distribution. In character, these occurrences were similar to new particle formation (NPF) events documented in the literature in a variety of locations worldwide [Hallar *et al.*, 2011; Kulmala *et al.*, 2004b]. Boy *et al.* [2008] presented analysis of NPF events observed at the University of Colorado Mountain Research Station, located about 100 km northwest of the Manitou Experimental Forest at an elevation of 2900 m. They divided days which showed clear NPF into two categories, A and B, both of which showed nucleation and growth of the new particles. For A events, nucleation mode particles (3–20 nm) were clearly observed at the initiation of the event. For B events, particles smaller than 6 nm were not present, but particles >6 nm were observed. They hypothesized that for B events nucleation began upwind with subsequent particle growth as the aerosol population was transported to the site. Finally, cases characterized by a sharp increase in particle concentration but little or no detectable growth were labeled as C, or undefined, events. We observed cases similar to A, B, and C events during our study.

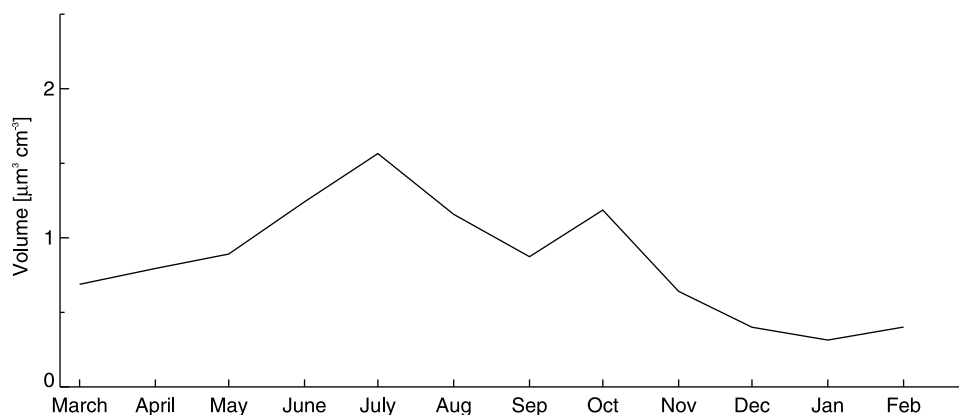


Figure 5. Monthly median aerosol volume concentrations, $14 < D_p < 350$ nm.

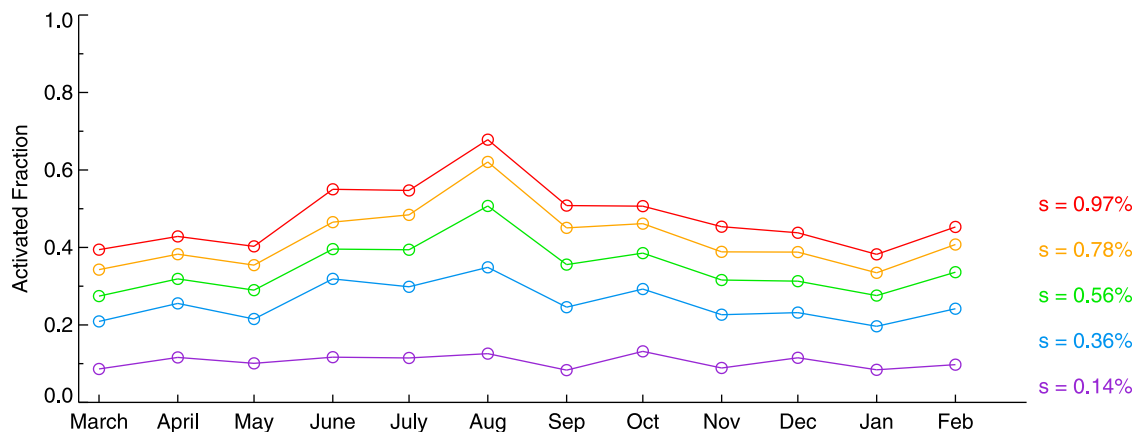


Figure 6. Monthly averaged activated fractions.

However, our measurements do not extend to small enough particle sizes to identify new particle nucleation, and thus we are unable to distinguish between A and B events. Because we cannot detect new particle nucleation, and thus clearly classify our events, we will use the term “small particle event” (SPE) to discuss these observations. *Boy et al.* [2008] also observed higher concentrations of mono- and sesquiterpenes during times of NPF and hypothesized that these organic compounds were important for particle growth. Although these compounds were not measured during our yearlong study, these BVOCs previously were shown to be emitted at or upwind of the BEACHON site by *Kim et al.* [2010]. *Riipinen et al.* [2011] also showed that organic species were important in growing new particles to CCN sizes and noted the importance of biogenic organic species in this process during the summer months, when biogenic and photochemical processes are most active.

[29] Figure 8 shows aerosol number concentrations during a SPE in April 2010. In this example, typical of these events, there was a burst in particle number concentration at the smallest measured diameters in the late morning of April 14, and these particles then grew, within ~ 12 h, into the accumulation mode. The sharp dip in aerosol concentration seen in Figure 8 just prior to the event may represent a change in

air mass at the site, or rapid dilution of the ambient air by mixing from aloft; however, there was not a clear change in wind speed or wind direction just prior to the SPE. Because it is unclear whether we may assume that conditions before and during the event represent the continuous evolution of the same aerosol, in the following we examine changes in aerosol hygroscopicity and CCN concentration only during the SPE itself.

[30] Figure 9 shows the total number concentration ($14 < D_p < 350$ nm) during this same time period, determined from our CPC measurements, as well as CCN concentrations at each s setting. As expected, there was a very large increase in total aerosol concentration during the event, increasing from less than $500\text{--}4500\text{ cm}^{-3}$. The concentration of CCN also increased, although there was a time lag in the increase of CCN number concentrations as the particles must grow large enough to activate (see Table 1 for typical activation diameters). At $s = 0.14\%$ there was little increase in CCN concentration during this event.

[31] While this event led to increases in aerosol and CCN concentrations, it had only a small effect on κ . Figure 10 shows κ at each s during this same time period. At the three highest s settings, κ remained consistently low throughout the event, suggesting that the event did not significantly alter

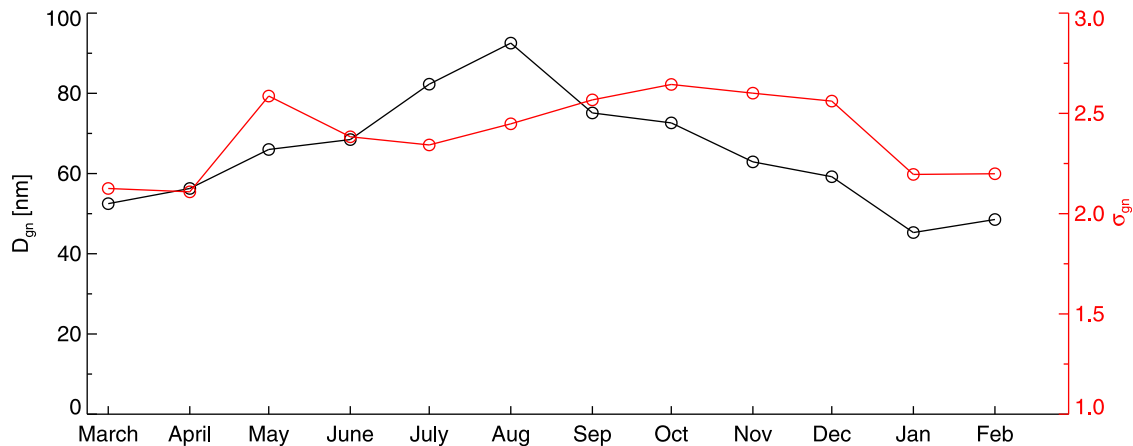


Figure 7. Geometric mean diameters (black) and geometric standard deviations (red) for the monthly averaged aerosol number distributions, $14 < D_p < 350$ nm.

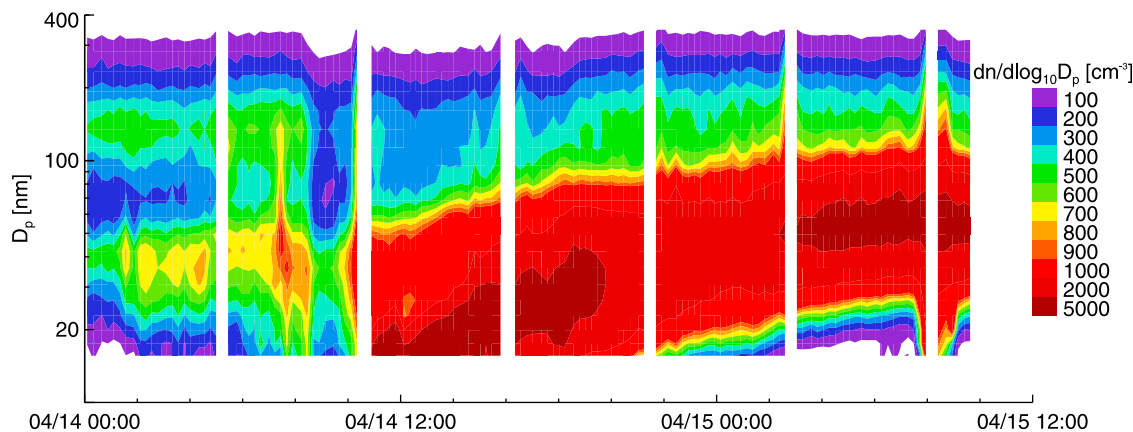


Figure 8. Aerosol number distribution evolution during a small particle event.

the chemical composition at these sizes. Kappa values at these sizes were also similar to those measured before the event. Therefore, even if there was an air mass change prior to the SPE, this did not correspond to a chemical change in the aerosol at the smaller sizes. Given the low κ values, it is likely that the smallest sampled particles were dominated by SOA both before and after the SPE. However, at the lowest supersaturations there was a decrease in κ as the new particles grew to sizes large enough to activate (Table 1), suggesting an important compositional effect for these larger particles.

[32] Small particle events were observed throughout the year but occurred most frequently in the summer. From July through September, SPEs occurred on 64% of the days for which we have data. During February, this number dropped to 11%. These more frequent SPEs in the summer are likely a main cause for the increased aerosol number concentrations during this time. Figure 11 shows monthly averaged total number and CCN concentrations plotted against the percentage of days with SPEs in that month. There is a clear positive trend in total number concentration as would be expected if these events are due to new particle formation. This increase in aerosol concentration also led, eventually, to an increase in mean diameter (Figure 12), likely resulting either from particle coagulation or condensation of volatile

vapors onto new particles, or both. Since SPEs are correlated with both increases in aerosol number concentration and mean diameter, CCN concentrations also increased as the percentage of days with SPEs increased (Figure 11). At $s = 0.14\%$, however, there was only a small increase in the number of CCN. As seen in the example case above, SPEs led to minimal increases in CCN concentrations at low s .

[33] In addition to affecting aerosol number concentration and mean diameter, SPEs also appeared to impact aerosol hygroscopicity at larger activation diameters. Figure 13 shows monthly averaged κ values plotted against the monthly percentage of days with SPEs. There is a clear decrease in κ at low s settings as the number of SPEs increases. For the higher s settings, there is no change in κ . Again, this is consistent with the event shown above in which we saw that at the smaller sizes there was no change in κ , and thus chemical composition, during an SPE. At the larger sizes, however, SPEs seem to increase the fraction of the aerosol population composed of lower κ species, likely organics. These particles' low hygroscopicity values led to the decreased κ values during times of high SPE. It must be noted that condensation of organic vapors onto preexisting particles may lower κ ; however, it will also increase the particle diameter. If κ of the condensing material is greater than 0 this increase in size will lead to an increase in CCN concentration at a given s

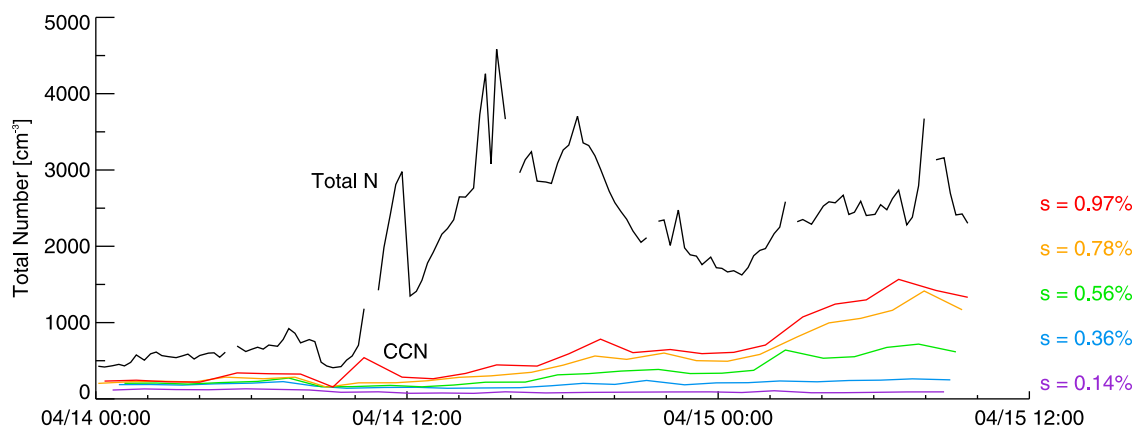


Figure 9. Total aerosol, $14 < D_p < 350$ nm (black), and CCN (colored) concentrations during a small particle event.

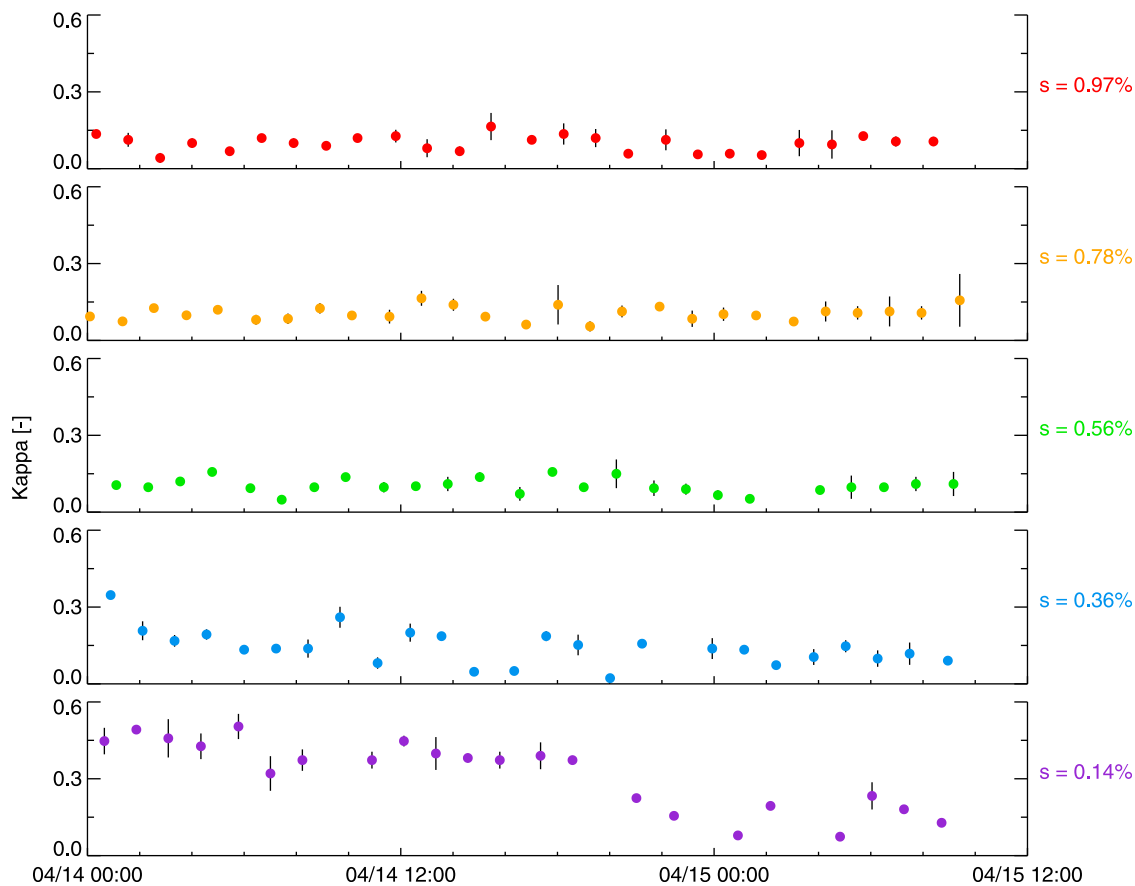


Figure 10. Kappa values at each supersaturation setting during a small particle event. Bars (smaller than symbols for most points) represent uncertainty in κ from curve fitting.

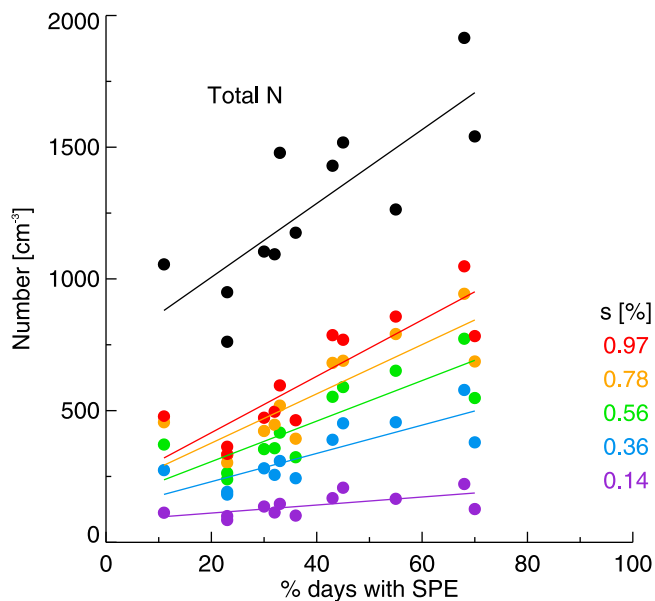


Figure 11. Monthly averaged aerosol number, $14 < D_p < 350$ nm (black), and CCN (colored) concentrations plotted against the percentage of days with small particle events in each month.

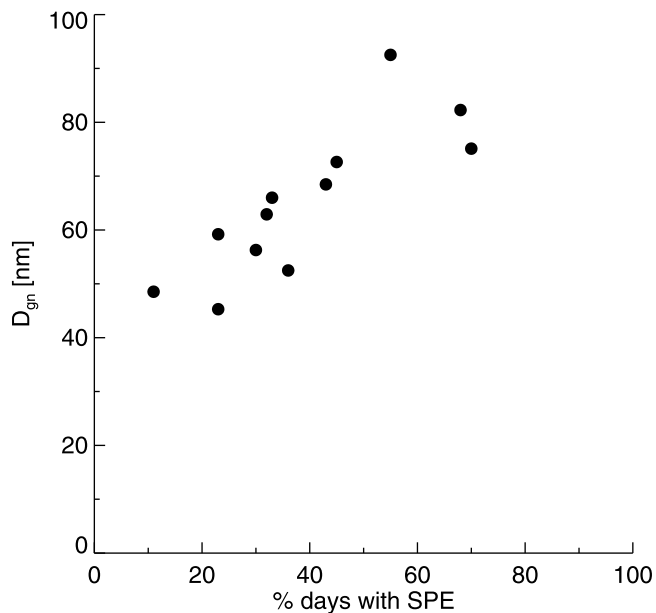


Figure 12. Monthly averaged aerosol number distribution geometric mean diameter plotted against the percentage of days with small particle events in each month.

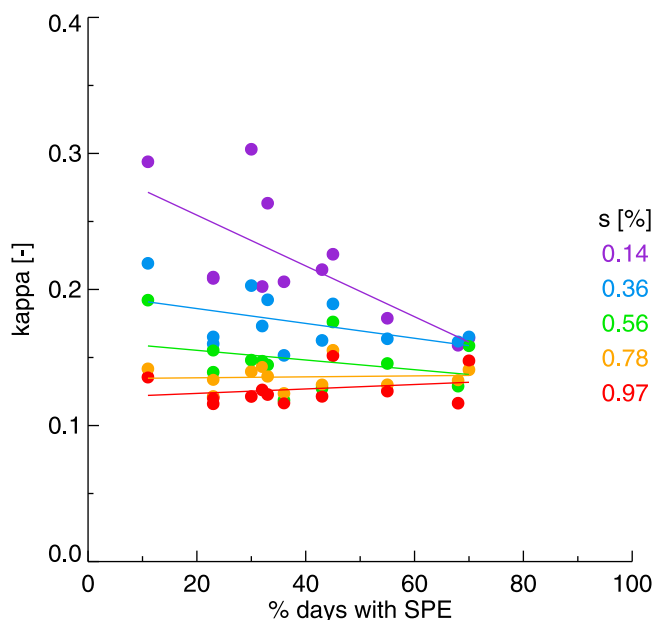


Figure 13. Monthly averaged κ values plotted against the percentage of days with small particle events in each month.

even if the overall hygroscopicity of the particle decreases. For condensing material with $\kappa = 0$, the decrease in particle hygroscopicity will be offset by the increase in size and lead to no change in CCN (see supplemental material for proof).

3.5. Tower Inlet

[34] All of the data reported thus far were from measurements made ~ 3 m AGL. We also sampled from an inlet ~ 25 m AGL from 12 May through 5 June 2011 to determine whether measurements made near the ground were representative of particles above the canopy. While this inlet height was still well below typical cloud base, it was above the forest canopy and may better represent the characteristics of the aerosol being entrained into clouds, and thus affecting cloud and precipitation formation and development.

[35] Very little difference was observed between measurements taken from the two inlets. Averaged over the entire tower measurement period and all s settings, $\kappa = 0.18 \pm 0.11$, while the average κ from the 3 m inlet from May to June 2010 was 0.19 ± 0.09 . It must be remembered that we had poor data coverage during May–June 2010 and thus the time periods between the tower and low inlet measurements do not match perfectly. Comparisons between average κ values at each s setting are shown in Table 2. Mean κ values were statically different for three of the s settings (indicated in boldface in Table 2), but the differences in these values were small. These similar hygroscopic properties measured above and below the forest canopy give validity to determining CCN hygroscopicity at ground level, at least for this site.

4. Summary and Conclusions

[36] Atmospheric particles, particularly those that act as CCN, are important in controlling cloud and precipitation formation and lifetime, and can have significant effects on local ecosystems and global climate. Secondary organic particles are particularly important in linking the biosphere,

hydrosphere and atmosphere together through these cloud interactions. Thus, the goal of this study, a part of the much larger BEACHON program, was to investigate the concentrations, CCN activity and seasonal variability of these particles. To this end, we measured size resolved CCN concentrations at a forested, mountainous site for 1 year from March 2010 through February 2011. Measurements were performed at five different supersaturation settings between 0.14% and 0.97% and across the size range 14–350 nm. We used the size resolved CCN activation curves at several set point supersaturations inside the CCNC to determine the hygroscopicity of the particles.

[37] Over the entire study, and all s settings, κ had an average value of 0.16 ± 0.08 , similar to values determined in both a tropical forest in the Amazon [Gunthe *et al.*, 2009; Poschl *et al.*, 2010] and a boreal forest in Finland [Sihto *et al.*, 2010]. The relatively low κ values measured at these forested locations suggest a predominance and potential importance of organic species, which generally have low hygroscopicity [King *et al.*, 2010; Petters *et al.*, 2009b; Prenni *et al.*, 2007].

[38] We also observed some seasonality in κ , especially at larger activation diameters. At $s = 0.14\%$, κ decreased from 0.3 in April to 0.16 in July and September. The hygroscopic properties of smaller particles, determined from higher s measurements, showed very little seasonal change with values changing only between 0.12 and 0.16 at $s = 0.97\%$. These consistently low values suggest that there was little change in the aerosol composition at these sizes throughout the year. For the larger particles, however, there was an increase in the less hygroscopic fraction during the summer months.

[39] While some seasonal changes were observed in κ , much larger changes were seen in CCN concentrations. In general, increases in CCN concentrations followed those of total measured aerosol concentrations, peaking in July. There was, however, an interesting seasonal change in the fraction of total aerosol that activated as CCN. Activated fraction increased during the summer, increasing from 38% in March to 68% in August at the highest s . This increase appears counterintuitive since aerosol hygroscopicity actually decreased during the summer. However, average aerosol number distributions shifted toward larger sizes during the summer, allowing more particles to activate as CCN despite their slightly depressed hygroscopic properties. This finding further highlights the importance of aerosol size in determining CCN concentrations [Dusek *et al.*, 2006].

[40] Small particle events, indicative of new particle formation, were observed throughout the study and appeared to

Table 2. Average κ Values Measured From the Ground (3 m) and Tower (25 m) Inlets^a

ΔT (°C)	κ at 3 m	κ at 25 m
4	0.25 ± 0.1	0.25 ± 0.1
8	0.19 ± 0.07	0.20 ± 0.07
12	0.14 ± 0.05	0.18 ± 0.06
16	0.14 ± 0.05	0.14 ± 0.05
19	0.13 ± 0.04	0.15 ± 0.04

^aSymbol \pm indicates 1 standard deviation. Ground-based measurements are for May–June 2010, while tower measurements were made May–June 2011. Boldface indicates statistically significant difference at the 95% confidence level.

affect both aerosol chemical and physical properties, and thus CCN concentrations. These events occurred year-round, but with higher frequency during the summer. These events led to large increases in aerosol number concentrations and, after the particles had grown large enough, increases in CCN concentrations. Small particle events also eventually led to increases in aerosol mean diameter, even though the particles started out at very small sizes. As well as these physical impacts, these small particle events were associated with some chemical changes in the aerosol. For the largest particle sizes measured, κ decreased as the frequency of SPEs increased. Because of the remote, forested location of our measurements, it is likely that the new particles were predominantly biogenic secondary organic species [Dusek et al., 2010; Kim et al., 2010]. For the smaller particles, determined from higher s measurements, however, there was no change in κ with increasing new particle formation. Aerosol composition at these sizes appeared to be persistently dominated by organics and, therefore, the new particles led to no hygroscopicity changes.

[41] Although we did not make direct measurements of aerosol composition, aerosol hygroscopicity suggests that particles smaller than 350 nm were dominated by organic species year-round at Manitou Experimental Forest, although at the largest sizes the apparent organic fraction did decrease in the winter. Further, small particle events were a main contributor, possibly the largest contributor, to the large increases in CCN concentration during the summer. Even in the winter, when emissions of BVOCs are expected to be lower [Lerdau et al., 1997], the smaller particles still appeared to be dominated by organic compounds. While compositional analysis is needed to completely understand the aerosol characteristics at the BEACHON measurement site, the CCN measurements presented here show a surprising similarity to those in highly biologically active locations such as the Amazon [Gunthe et al., 2009; Poschl et al., 2010]. Thus, even in this semiarid, high-altitude location, organic aerosol particles, likely of biological origin, are important in linking the biosphere, hydrosphere and atmosphere.

[42] **Acknowledgments.** This work is funded by NSF (ATM-0919042). We thank David C. Rogers for the use of one of the 3010 CPCs deployed during this study. The National Center for Atmospheric Research is sponsored by the U.S. National Science Foundation. J.N.S. acknowledges the financial support of the Saastamoinen Foundation.

References

- Albrecht, B. A. (1989), Aerosols, cloud microphysics, and fractional cloudiness, *Science*, *245*, 1227–1230, doi:10.1126/science.245.4923.1227.
- Andreae, M. O., and D. Rosenfeld (2008), Aerosol-cloud-precipitation interactions. Part I. The nature and sources of cloud-active aerosols, *Earth Sci. Rev.*, *89*, 13–41, doi:10.1016/j.earscirev.2008.03.001.
- Andreae, M. O., et al. (2002), Biogeochemical cycling of carbon, water, energy, trace gases, and aerosols in Amazonia: The LBA-EUSTACH experiments, *J. Geophys. Res.*, *107*(D20), 8066, doi:10.1029/2001JD000524.
- Asa-Awuku, A., G. J. Engelhart, B. H. Lee, S. N. Pandis, and A. Nenes (2009), Relating CCN activity, volatility, and droplet growth kinetics of beta-caryophyllene secondary organic aerosol, *Atmos. Chem. Phys.*, *9*, 795–812, doi:10.5194/acp-9-795-2009.
- Asa-Awuku, A., A. Nenes, S. Gao, R. C. Flagan, and J. H. Seinfeld (2010), Water-soluble SOA from alkene ozonolysis: Composition and droplet activation kinetics inferences from analysis of CCN activity, *Atmos. Chem. Phys.*, *10*, 1585–1597, doi:10.5194/acp-10-1585-2010.
- Barth, M., et al. (2005), Coupling between land ecosystems and the atmospheric hydrologic cycle through biogenic aerosol pathways, *Bull. Am. Meteorol. Soc.*, *86*, 1738–1742, doi:10.1175/BAMS-86-12-1738.
- Boy, M., et al. (2008), New particle formation in the front range of the Colorado Rocky Mountains, *Atmos. Chem. Phys.*, *8*, 1577–1590, doi:10.5194/acp-8-1577-2008.
- Cerully, K. M., et al. (2011), Aerosol hygroscopicity and CCN activation kinetics in a boreal forest environment during the 2007 EUCAARI campaign, *Atmos. Chem. Phys. Discuss.*, *11*, 15,029–15,074, doi:10.5194/acpd-11-15029-2011.
- Clegg, S. L., and P. Brimblecombe (1998), Thermodynamic model of the system $\text{H}^+ - \text{NH}_4^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{H}_2\text{O}$ at tropospheric temperatures, *J. Phys. Chem. A*, *102*, 2137–2154, doi:10.1021/jp973042r.
- Draxler, R. R. (1999), *HYSPLIT4 User's Guide*, NOAA Air Resour. Lab., Silver Spring, Md.
- Draxler, R. R., and G. D. Hess (1997), Description of the HYSPLIT_4 modeling system, report, 24 pp., NOAA Air Resour. Lab., Silver Spring, Md.
- Draxler, R. R., and G. D. Hess (1998), An overview of the HYSPLIT_4 modeling system of trajectories, dispersion, and deposition, *Aust. Meteorol. Mag.*, *47*, 295–308.
- Duhl, T. R., D. Helmig, and A. Guenther (2008), Sesquiterpene emissions from vegetation: A review, *Biogeosciences*, *5*, 761–777, doi:10.5194/bg-5-761-2008.
- Duplissy, J., et al. (2008), Cloud forming potential of secondary organic aerosol under near atmospheric conditions, *Geophys. Res. Lett.*, *35*, L03818, doi:10.1029/2007GL031075.
- Dusek, U., et al. (2006), Size matters more than chemistry for cloud-nucleating ability of aerosol particles, *Science*, *312*, 1375–1378, doi:10.1126/science.1125261.
- Dusek, U., et al. (2010), Enhanced organic mass fraction and decreased hygroscopicity of cloud condensation nuclei (CCN) during new particle formation events, *Geophys. Res. Lett.*, *37*, L03804, doi:10.1029/2009GL040930.
- Engelhart, G. J., R. H. Moore, A. Nenes, and S. N. Pandis (2011), Cloud condensation nuclei activity of isoprene secondary organic aerosol, *J. Geophys. Res.*, *116*, D02207, doi:10.1029/2010JD014706.
- Fors, E. O., E. Swietlicki, B. Svenningsson, A. Kristensson, G. P. Frank, and M. Sporre (2011), Hygroscopic properties of the ambient aerosol in southern Sweden—A two year study, *Atmos. Chem. Phys.*, *11*, 8343–8361, doi:10.5194/acp-11-8343-2011.
- Fuzzi, S., et al. (2006), Critical assessment of the current state of scientific knowledge, terminology, and research needs concerning the role of organic aerosols in the atmosphere, climate, and global change, *Atmos. Chem. Phys.*, *6*, 2017–2038, doi:10.5194/acp-6-2017-2006.
- Gunthe, S. S., et al. (2009), Cloud condensation nuclei in pristine tropical rainforest air of Amazonia: Size-resolved measurements and modeling of atmospheric aerosol composition and CCN activity, *Atmos. Chem. Phys.*, *9*, 7551–7575, doi:10.5194/acp-9-7551-2009.
- Hallar, A. G., D. H. Lowenthal, G. Chirokova, R. D. Borys, and C. Wiedinmyer (2011), Persistent daily new particle formation at a mountain-top location, *Atmos. Environ.*, *45*, 4111–4115, doi:10.1016/j.atmosenv.2011.04.044.
- Jimenez, J. L., et al. (2009), Evolution of organic aerosols in the atmosphere, *Science*, *326*, 1525–1529, doi:10.1126/science.1180353.
- Kammermann, L., M. Gysel, E. Weingartner, and U. Baltensperger (2010), 13-month climatology of the aerosol hygroscopicity at the free tropospheric site Jungfraujoch (3580 m a.s.l.), *Atmos. Chem. Phys.*, *10*, 717–732, doi:10.5194/acp-10-717-2010.
- Kanakidou, M., et al. (2005), Organic aerosol and global climate modelling: A review, *Atmos. Chem. Phys.*, *5*, 1053–1123, doi:10.5194/acp-5-1053-2005.
- Kim, S., T. Karl, A. Guenther, G. Tyndall, J. Orlando, P. Harley, R. Rasmussen, and E. Apel (2010), Emissions and ambient distributions of biogenic volatile organic compounds (BVOC) in a ponderosa pine ecosystem: Interpretation of PTR-MS mass spectra, *Atmos. Chem. Phys.*, *10*, 1759–1771, doi:10.5194/acp-10-1759-2010.
- King, S. M., T. Rosenoern, J. E. Shilling, Q. Chen, and S. T. Martin (2007), Cloud condensation nucleus activity of secondary organic aerosol particles mixed with sulfate, *Geophys. Res. Lett.*, *34*, L24806, doi:10.1029/2007GL030390.
- King, S. M., T. Rosenoern, J. E. Shilling, Q. Chen, Z. Wang, G. Biskos, K. A. McKinney, U. Pöschl, and S. T. Martin (2010), Cloud droplet activation of mixed organic-sulfate particles produced by the photooxidation of isoprene, *Atmos. Chem. Phys.*, *10*, 3953–3964, doi:10.5194/acp-10-3953-2010.
- Kulmala, M., et al. (2004a), A new feedback mechanism linking forests, aerosols, and climate, *Atmos. Chem. Phys.*, *4*, 557–562, doi:10.5194/acp-4-557-2004

- Kulmala, M., H. Vehkamäki, T. Petäjä, M. Dal Maso, A. Lauri, V.-M. Kerminen, W. Birmili, and P. H. McMurry (2004b), Formation and growth rates of ultrafine atmospheric particles: A review of observations, *J. Aerosol Sci.*, *35*, 143–176, doi:10.1016/j.jaerosci.2003.10.003.
- Lerdau, M., et al. (1997), Controls over monoterpene emissions from boreal forest conifers, *Tree Physiol.*, *17*, 563–569.
- Levin, E. J. T., S. M. Kreidenweis, G. R. McMeeking, C. M. Carrico, J. L. Collett Jr., and W. C. Malm (2009), Aerosol physical, chemical and optical properties during the Rocky Mountain Airborne Nitrogen and Sulfur study, *Atmos. Environ.*, *43*, 1932–1939, doi:10.1016/j.atmosenv.2008.12.042.
- Malm, W. C., J. F. Sisler, D. Huffman, R. A. Eldred, and T. A. Cahill (1994), Spatial and seasonal trends in particle concentrations and optical extinction in the United States, *J. Geophys. Res.*, *99*, 1347–1370, doi:10.1029/93JD02916.
- Malm, W. C., B. A. Schichtel, M. L. Pitchford, L. L. Ashbaugh, and R. A. Eldred (2004), Spatial and monthly trends in speciated fine particle concentration in the United States, *J. Geophys. Res.*, *109*, D03306, doi:10.1029/2003JD003739.
- Massoli, P., et al. (2010), Relationship between aerosol oxidation level and hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles, *Geophys. Res. Lett.*, *37*, L24801, doi:10.1029/2010GL045258.
- Petters, M. D., and S. M. Kreidenweis (2007), A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, *Atmos. Chem. Phys.*, *7*, 1961–1971, doi:10.5194/acp-7-1961-2007.
- Petters, M. D., A. J. Prenni, S. M. Kreidenweis, and P. J. DeMott (2007), On measuring the critical diameter of cloud condensation nuclei using mobility selected aerosol, *Aerosol Sci. Technol.*, *41*, 907–913, doi:10.1080/02786820701557214.
- Petters, M. D., C. M. Carrico, S. M. Kreidenweis, A. J. Prenni, P. J. DeMott, J. L. Collett Jr., and H. Moosmüller (2009a), Cloud condensation nucleation activity of biomass burning aerosol, *J. Geophys. Res.*, *114*, D22205, doi:10.1029/2009JD012353.
- Petters, M. D., S. M. Kreidenweis, A. J. Prenni, R. C. Sullivan, C. M. Carrico, K. A. Koehler, and P. J. Ziemann (2009b), Role of molecular size in cloud droplet activation, *Geophys. Res. Lett.*, *36*, L22801, doi:10.1029/2009GL040131.
- Poschl, U., et al. (2010), Rainforest aerosols as biogenic nuclei of clouds and precipitation in the Amazon, *Science*, *329*, 1513–1516, doi:10.1126/science.1191056.
- Poullain, L., Z. Wu, M. D. Petters, H. Wex, E. Hallbauer, B. Wehner, A. Massling, S. M. Kreidenweis, and F. Stratmann (2010), Towards closing the gap between hygroscopic growth and CCN activation for secondary organic aerosols—Part 3: Influence of the chemical composition on the hygroscopic properties and volatile fractions of aerosols, *Atmos. Chem. Phys.*, *10*, 3775–3785, doi:10.5194/acp-10-3775-2010.
- Prenni, A. J., M. D. Petters, S. M. Kreidenweis, P. J. DeMott, and P. J. Ziemann (2007), Cloud droplet activation of secondary organic aerosol, *J. Geophys. Res.*, *112*, D10223, doi:10.1029/2006JD007963.
- Riipinen, I., et al. (2011), Organic condensation: A vital link connecting aerosol formation to cloud condensation nuclei (CCN) concentrations, *Atmos. Chem. Phys.*, *11*, 3865–3878, doi:10.5194/acp-11-3865-2011.
- Roberts, G. C., and A. Nenes (2005), A continuous-flow streamwise thermal-gradient CCN chamber for atmospheric measurements, *Aerosol Sci. Technol.*, *39*, 206–221, doi:10.1080/027868290913988.
- Robinson, N. H., et al. (2011), Evidence for a significant proportion of secondary organic aerosol from isoprene above a maritime tropical forest, *Atmos. Chem. Phys.*, *11*, 1039–1050, doi:10.5194/acp-11-1039-2011.
- Rose, D., S. S. Gunthe, E. Mikhailov, G. P. Frank, U. Dusek, M. O. Andreae, and U. Pöschl (2008), Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment, *Atmos. Chem. Phys.*, *8*, 1153–1179, doi:10.5194/acp-8-1153-2008.
- Rosenfeld, D., U. Lohmann, G. B. Raga, C. D. O’Dowd, M. Kulmala, S. Fuzzi, A. Reissell, and M. O. Andreae (2008), Flood or drought: How do aerosols affect precipitation?, *Science*, *321*, 1309–1313, doi:10.1126/science.1160606.
- Schichtel, B. A., W. C. Malm, G. Bench, S. Fallon, C. E. McDade, J. C. Chow, and J. G. Watson (2008), Fossil and contemporary fine particulate carbon fractions at 12 rural and urban sites in the United States, *J. Geophys. Res.*, *113*, D02311, doi:10.1029/2007JD008605.
- Sharkey, T. D., A. E. Wiberley, and A. R. Donohue (2007), Isoprene emission from plants: Why and how, *Ann. Bot.*, *101*, 5–18, doi:10.1093/aob/mcm240.
- Sihto, S.-L., et al. (2010), Seasonal variation of CCN concentrations and aerosol activation properties in boreal forest, *Atmos. Chem. Phys. Discuss.*, *10*, 28,231–28,272, doi:10.5194/acpd-10-28231-2010.
- Telford, P. J., et al. (2010), Effects of climate-induced changes in isoprene emissions after the eruption of Mount Pinatubo, *Atmos. Chem. Phys.*, *10*, 7117–7125, doi:10.5194/acp-10-7117-2010.
- Twomey, S. (1974), Pollution and planetary albedo, *Atmos. Environ.*, *8*, 1251–1256, doi:10.1016/0004-6981(74)90004-3.
- Zhang, Q., et al. (2007), Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically influenced Northern Hemisphere midlatitudes, *Geophys. Res. Lett.*, *34*, L13801, doi:10.1029/2007GL029979.

S. A. Atwood, P. J. DeMott, S. M. Kreidenweis, E. J. T. Levin, A. J. Prenni, and R. C. Sullivan, Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80523, USA. (elevin@atmos.colostate.edu)
 J. Ortega and J. N. Smith, Atmospheric Chemistry Division, National Center for Atmospheric Research, PO Box 3000, Boulder, CO 80307, USA.
 M. D. Petters, Marine Earth and Atmospheric Sciences, North Carolina State University, Campus Box 8208, Raleigh, NC 27695, USA.