



CCN activity of organic aerosols observed downwind of urban emissions during CARES

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Abstract. During the Carbonaceous Aerosols and Radiative Effects Study (CARES), activation fraction of size-resolved aerosol particles and aerosol chemical composition were characterized at the T1 site (~60 km downwind of Sacramento, California) from 10 June to 28 June 2010. The hygroscopicity of cloud condensation nuclei (CCN)-active particles (κ_{CCN}) with diameter from 100 to 170 nm, derived from the size-resolved activated fraction, varied from 0.10 to 0.21, with an average of 0.15, which was substantially lower than that proposed for continental sites. The low κ_{CCN} value was due to the high organic volume fraction, averaged over 80% at the T1 site. The derived κ_{CCN} exhibited little diurnal variation, consistent with the relatively constant organic volume fraction observed. At any time, over 90% of the size-selected particles with diameter between 100 and 171 nm were CCN active, suggesting most particles within this size range were aged background particles. Due to the large organic volume fraction, organic hygroscopicity (κ_{org}) strongly impacted particle hygroscopicity and therefore calculated CCN concentration. For the vast majority of the cases, an increase of κ_{org} from 0.03 to 0.18, which are within the typical range, doubled the calculated CCN concentration. Organic hygroscopicity was derived from κ_{CCN} and aerosol chemical composition, and its variations with the fraction of total organic mass spectral signal at m/z 44 (f_{44}) and O:C were compared to results from previous studies. Overall, the relationships between κ_{org} and f_{44} are quite consistent for organic aerosol (OA) observed during field stud-

ies and those formed in a smog chamber. Compared to the relationship between κ_{org} and f_{44} , the relationship between κ_{org} and O:C exhibits more significant differences among different studies, suggesting κ_{org} may be better parameterized using f_{44} . A least squares fit yielded $\kappa_{\text{org}} = 2.10(\pm 0.07) \times f_{44} - 0.11(\pm 0.01)$ with a Pearson R^2 value of 0.71. One possible explanation for the stronger correlation between κ_{org} and f_{44} is that the m/z 44 signal (mostly contributed by the CO_2^+ ion) is more closely related to organic acids, which may dominate the overall κ_{org} due to their relatively high water solubility and hygroscopicity.

1 Introduction

Atmospheric aerosols influence the global energy budget indirectly by changing the microphysical structure, lifetime, and coverage of clouds. An increase in aerosol concentration leads to smaller cloud droplet size and higher cloud albedo (i.e., first indirect effect; Twomey, 1977). The smaller droplet size also inhibits precipitation, leading to increases in both cloud lifetime and coverage (i.e., second indirect effect; Albrecht, 1989). Although it is generally agreed upon that indirect effects of aerosols tend to cool the Earth–atmosphere system by increasing cloud albedo, thickness, and coverage, the magnitudes of these effects are poorly understood, and the indirect effects of aerosols remain the most uncertain

components in forcing of climate change over the industrial period (IPCC, 2007).

Understanding aerosol indirect effects requires knowledge of the ability of aerosol particles to form cloud droplets at atmospherically relevant supersaturations (i.e., CCN activity).

The cloud condensation nuclei (CCN) activity of atmospheric particles can be effectively predicted using Köhler theory (Köhler, 1936), provided that the particle size and physicochemical properties of the solute – including its molar volume, activity coefficient, and effect on surface tension – are known (McFiggans et al., 2006). Several essentially equivalent single-parameter frameworks have been proposed to model the CCN activation and hygroscopicity of multi-component aerosols (Hudson and Da, 1996; Rissler et al., 2006; Petters and Kreidenweis, 2007, 2008; Wex et al., 2007). These single-parameter frameworks combine many of the thermodynamic details necessary for the description of water activity, and provide a more streamlined approach to represent CCN activation in models. Here we use the hygroscopicity parameter κ proposed by Petters and Kreidenweis (2007, 2008), which can be conveniently derived from size-resolved CCN measurements. Besides droplet activation, hygroscopicity also describes particle growth under subsaturated conditions and can be derived from particle growth factor (GF) measured by a humidified tandem differential mobility analyzer (HTDMA). Previous studies suggest particles may exhibit larger κ values for droplet activation (derived from CCN measurements under supersaturated conditions) than those for particle growth (derived from particle GF under subsaturated conditions) (Duplissy et al., 2008; Wex et al., 2008, 2009; Petters et al., 2009b; Good et al., 2010). In this paper, unless otherwise noted, “hygroscopicity” refers to κ associated with droplet activation under supersaturated conditions.

The hygroscopicities of ambient inorganic species are relatively well known. In contrast, atmospheric aerosols often contain hundreds of organic species, which can contribute ~20–90% to the total fine aerosol mass (Kanakidou et al., 2005; Zhang et al., 2007). A number of studies have examined the hygroscopicity of organic aerosols, including laboratory-generated organic aerosols with known composition (e.g., Raymond and Pandis, 2002, 2003; Pradeep Kumar et al., 2003; Bilde and Svenningsson, 2004; Abbatt et al., 2005; Huff-Hartz et al., 2006; Svenningsson et al., 2006), secondary organic aerosols (SOA) generated in controlled environmental chambers (Prenni et al., 2007; Duplissy et al., 2008, 2011; Asa-Awuku et al., 2009; King et al., 2009; Masoli et al., 2010; Lambe et al., 2011), and aerosols generated in laboratory biomass burning experiments (Petters et al., 2009a). A number of field studies also reported the range of κ for the organic component of ambient aerosols (Wang et al., 2008; Shantz et al., 2008; Gunthe et al., 2009; Chang et al., 2010; Jimenez et al., 2009; Mei et al., 2013; Rose et al., 2010). Collectively, the laboratory and field studies suggest that organics have a fairly wide range of κ values ranging

from 0 to 0.3, and κ_{org} can increase substantially during their chemical aging in the atmosphere (Jimenez et al., 2009; Masoli et al., 2010; Duplissy et al., 2011; Lambe et al., 2011; Mei et al., 2013).

The sensitivity of predicted CCN concentration and droplet number concentration to aerosol properties, including the hygroscopicity of organic species, are examined in a number of recent studies (Rissman et al., 2004; McFiggans et al., 2006; Wang et al., 2008; Reutter et al., 2009; Ervens et al., 2010; Kammermann et al., 2010; Ward et al., 2010; Wang, 2007). While these studies all recognize the importance of particle size distribution, mixing state, and volume fraction of organics in particles, they also indicate that the predicted CCN concentration and droplet number concentration can be sensitive to κ_{org} , and the value of κ_{org} needed to reproduce measured CCN concentration can vary substantially, and depends on the location and time of the study. Using constant κ for organic components may lead to significant biases in predicted CCN concentrations and aerosol indirect forcing (Liu and Wang, 2010). On the other hand, atmospheric aerosols often contain hundreds of organic species, and the hygroscopicities of many organic species are often not available. Therefore efficient parameterizations that can capture the major variation of κ_{org} are essential for implementation in large-scale models. One promising idea is that the κ_{org} under both supersaturated and subsaturated conditions may be parameterized based on the organic oxidation level (e.g., O:C atomic ratio), which can be measured by aerosol mass spectrometers (Aiken et al., 2008) and other techniques. For particle hygroscopic growth under subsaturated conditions, measurements from TDMA show that κ_{org} increases with O:C for a number of organic aerosols (Jimenez et al., 2009; Duplissy et al., 2011). Positive correlations between κ_{org} and O:C were also found under supersaturated conditions for SOA and oxidized POA generated in a Potential Aerosol Mass (PAM) flow reactor (Masoli et al., 2010; Lambe et al., 2011), and ambient organic aerosols observed at rural (Chang et al., 2010) and urban (Mei et al., 2013) sites. At present, the data on the hygroscopicity of ambient organics are still quite limited (Latham et al., 2013; Moore et al., 2011), and the relationship between κ_{org} and organic oxidation level needs to be examined for ambient aerosols from representative organic aerosol sources before it can be confidently implemented in climate models. In this paper we report particle hygroscopicity and mixing state derived from size-resolved CCN measurements carried out during the Carbonaceous Aerosol and Radiative Effects Study (CARES). The impact of κ_{org} on predicted CCN spectrum was examined. Organic hygroscopicity was derived from particle hygroscopicity and chemical composition, and its relationship to organics oxidation level is discussed.

2 Experimental method

2.1 Measurement site

The Carbonaceous Aerosol and Radiative Effects Study was a field campaign focusing on the evolution of secondary organic and black carbon (BC) aerosols and their climate-related properties in the Sacramento urban plume as it was routinely transported into the forested Sierra Nevada foothills area (Zaveri et al., 2012). Aerosol measurements were taken from 2 June to 28 June 2010 at the T1 site, which was located about 60 km to the northeast of Sacramento in Cool, CA, a small town situated amidst a forested area rich in biogenic emissions (latitude: 38.87; longitude: -121.02 ; altitude: ~ 460 m m.s.l.). The data related to the analysis presented in this paper were available from 10 June to 28 June. Aerosol data included aerosol size distribution, chemical composition, CCN spectrum (as a function of supersaturation), size-resolved CCN spectrum and activated fraction, all of which were taken at the ground level. All measurements are reported at ambient conditions and local time (UTC time minus 7 h) is used throughout this study.

2.2 Size-resolved CCN activated fraction and total CCN spectrum

The measurement of size-resolved CCN activated fraction is detailed in Mei et al. (2013) and is briefly described here. Ambient aerosol was first dried to below 20 % relative humidity and neutralized by a Kr-85 aerosol neutralizer, and subsequently classified by a differential mobility analyzer. The classified aerosol was then simultaneously characterized by a condensation particle counter and a CCN counter (Roberts and Nenes, 2005; Lance et al., 2006; Rose et al., 2008). During CARES, the sample and sheath flows of the DMA were maintained at 0.8 and 8 L min⁻¹, respectively. The total flow of CPC was reduced to 0.5 L min⁻¹ and the sample flow of the CCN counter was maintained at 0.3 L min⁻¹. The measurement sequence is illustrated in Fig. S1 (Supplement). The longitudinal temperature gradients of the CCN counter was stepped through 4.5, 5.5, 6.5, 8, 10, 12 °C (Fig. S1b). Based on calibrations using ammonium sulfate particles, the corresponding supersaturations (*S*) derived from Köhler theory using a constant van't Hoff factor of 2.5 were 0.15 %, 0.19 %, 0.23 %, 0.30 %, 0.39 % and 0.45 %, respectively. The supersaturation inside the CCN counter was maintained at each value for approximately 40 min, during which the diameter of particles classified by the DMA was scanned between 20 nm and 350 nm eight times (310 s per scan) (Wang and Flagan, 1990). The CCN counter was stepped through the temperature gradients in a “sawtooth” pattern (Fig. S1b), and provided measurements at the above six *S* values approximately every 4 h. The aerosol size distribution was derived by inverting the particle concentration measured by the CPC using a routine described in Collins

et al. (2002). The same procedure was also applied to measured CCN concentration to obtain size-resolved CCN concentration. The ratio of the two provided size-resolved CCN activated fraction.

In addition to size-resolved CCN activated fraction, total CCN concentration was measured using a second CCN counter (Droplet Measurement Technologies, Model CCN-100) operated at a flow rate of 0.3 L min⁻¹, and longitudinal temperature gradients of 4.0, 5.5, 6.6, 8.1, and 10.3 °C, which corresponded to supersaturations 0.12 %, 0.20 %, 0.24 %, 0.30 %, and 0.38 %, respectively. The temperature gradient was stepped through the five values every 30 min as shown in Fig. S1a.

2.3 Chemical composition

The concentrations of submicron non-refractory (NR-PM₁) organic and inorganic (nitrate, sulfate, ammonium, chloride) aerosol species were measured using a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc., hereinafter AMS for short) (DeCarlo et al., 2006). The AMS sampled from an inlet equipped with a PM₁ impactor (Brechtel Manufacturing Inc., Hayward, CA; model 8003). The ambient air passed through 3 feet (0.91 m) of stainless steel tube with an inner diameter of 3/4 inch (1.91 cm), 8 feet (2.44 m) of copper tube with an inner diameter of 1/4 inch (0.64 cm), 2 feet (0.61 m) long temperature-controlled thermodenuder, and a Nafion dryer prior to sampling by the AMS. The resulting data were averaged over 2.5 min intervals. All data were analyzed using standard AMS software (SQUIRREL v1.51 and PIKA v1.10) within Igor Pro 6.2.2.2 (Wave Metrics, Lake Oswego, OR). Details of the AMS operation, data treatment, positive matrix factorization (PMF) analysis, and data interpretation are given elsewhere (Setyan et al., 2012).

3 Diurnal variations of aerosol properties

Diurnal variations of aerosol properties observed from 10 June to 28 June 2010 are shown in Fig. 1, including aerosol particle size distribution (Fig. 1a), species mass concentrations measured by the AMS (Fig. 1b), derived volume fractions of major species (Fig. 1c), and measured CCN concentrations (Fig. 1d). Sulfate and nitrate were essentially neutralized by ammonium in the CCN-relevant sizes (Setyan et al., 2012). The volume fractions of major species were calculated using densities of organics (1.25 g cm⁻³), ammonium sulfate (1.77 g cm⁻³), ammonium nitrate (1.72 g cm⁻³), and BC (1.8 g cm⁻³). The mass concentration of BC was typically less than 0.1 μg m⁻³, contributing to less than 2 % of the total submicron aerosol volume (not shown). High number concentration (*N*_{CCN}) of Aitken mode particles was often observed in the afternoon between 12:00 and 18:00, and is attributed to early morning traffic-hour pollution transported

from downtown Sacramento (Setyan et al., 2012). The mass concentration of sulfate and organics showed a relatively modest increase ($\sim 30\%$ over otherwise nearly constant background) during this period. However, the species volume fractions were relatively constant during the day. Among all the species, organics had by far the largest contribution to the total submicron aerosol volume, at $\sim 85\%$. The contributions from sulfate and nitrate were only $\sim 10\%$ and $\sim 5\%$, respectively. On average, CCN concentrations measured at 0.12% and 0.38% supersaturations were ~ 120 and $\sim 1000\text{ cm}^{-3}$. No significant diurnal trends in measured CCN concentrations were observed, suggesting most particles transported from the Sacramento area observed between 12:00 and 18:00 were not effective CCNs under measured supersaturations. This was likely due to the combination of the relatively small particle size (a majority of the particles transported to T1 during 12:00–18:00 were smaller than 50 nm in diameter) and particle compositions dominated by organics that in general are significantly less hygroscopic than inorganic salts such as sulfate.

4 Methods

4.1 Derivation of particle hygroscopicity and mixing state

The derivation of particle hygroscopicity κ and mixing state was detailed in Mei et al. (2013) and is briefly described here. The activated fraction of size-selected particles (R_a) typically increased with increasing supersaturation, and eventually reached a plateau, which gives the maximum activated fraction (E). The difference between 100% and E represents the number fraction of particles consisting of only non-hygroscopic species (e.g., BC) that cannot serve as CCN under typical atmospheric supersaturations. The characteristic critical supersaturation (S^*) of the size-selected CCN is the supersaturation at which R_a reaches 50% of E . The variation of R_a as a function of S was fitted using both a sigmoid function (Lance, 2007; Cerully et al., 2011; Bougiatioti et al., 2011; Padro et al., 2012; Lance et al., 2013; Mei et al., 2013) and a lognormal function (Mei et al., 2013), with E and S^* among fitting parameters. For each set of measurements, the function form that yielded the best fit (i.e., smaller least squares residue) was employed for subsequent analysis. The probability density function of the critical supersaturation for the size-selected CCN was derived by differentiating the fitted R_a with respect to S (Supplement). The density function was then used to calculate the dispersion of CCN hygroscopicity by taking into consideration the width of DMA transfer function (Mei et al., 2013; Lance et al., 2013). The dispersion of CCN hygroscopicity, which reflects the chemical heterogeneity of activated particles, is defined as $\sigma(\kappa)/\bar{\kappa}$, where $\sigma(\kappa)$ and $\bar{\kappa}$ are the standard deviation and the average of the

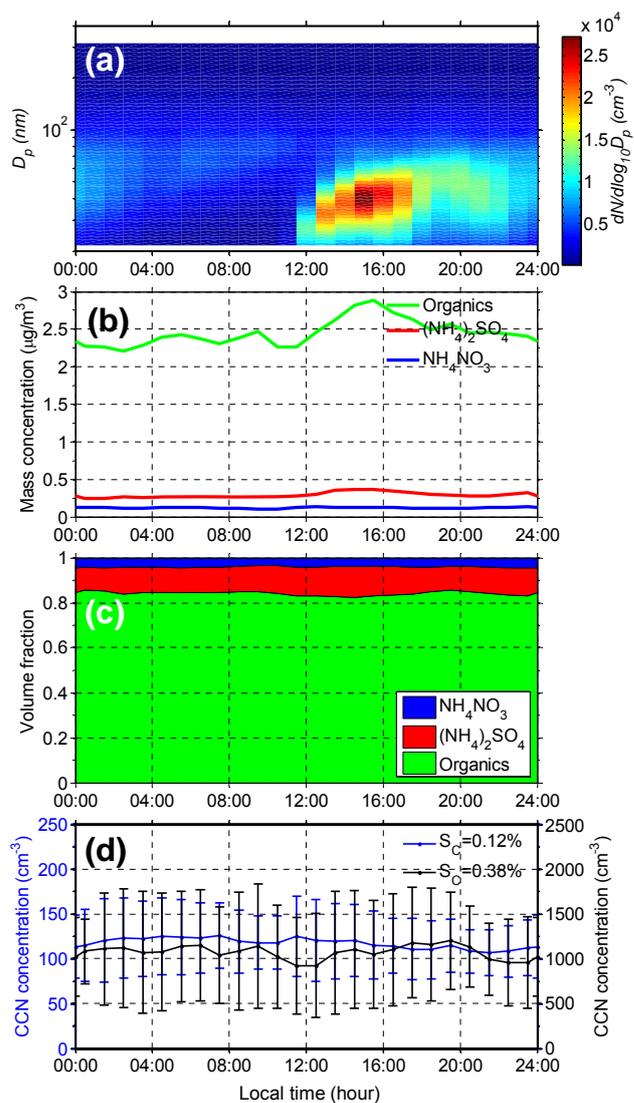


Fig. 1. Diurnal variations of aerosol properties observed at the T1 site from 10 June to 28 June 2012. (a) Aerosol size distribution; (b) mass concentrations and (c) volume fractions of organics, $(\text{NH}_4)_2\text{SO}_4$, and NH_4NO_3 ; and (d) CCN concentrations measured at supersaturations of 0.12% and 0.38%.

CCN hygroscopicity, respectively (Mei et al., 2013). The details of the derivations are also given in the Supplement.

4.2 Derivation of organic hygroscopicity and its uncertainty

Measurements from AMS show the composition of submicron particles was dominated by organics, followed by ammonium, sulfate, and nitrate (Fig. 1). The contribution of chloride was negligible, and the analysis of anion and cation balance suggests that anionic species (NO_3^- , SO_4^{2-}) were neutralized by NH_4^+ over the relevant size range of CCN measurements (Setyan et al., 2012). For refractory species,

BC represented a negligible fraction of the total submicron aerosol volume (i.e., less than 2%), and the contribution of sea salt and dust are also expected to be negligible for the size range of interest (i.e., less than 300 nm) at the T1 site. Therefore, aerosols within the size range examined were assumed consisting of the following three species: organics, $(\text{NH}_4)_2\text{SO}_4$, and NH_4NO_3 . We note that a fraction of nitrate observed was organonitrate or metal nitrate (Setyan et al., 2012). However, as nitrate only represented $\sim 3.5\%$ of total non-refractory PM_{10} , assuming nitrate as NH_4NO_3 should not substantially affect derived κ_{org} values. During CARES, E observed at the T1 site was mostly very close to 100% (the minimum E was 92% during the periods chosen for deriving κ_{org} as described below). Therefore, particles were assumed as internal mixtures, and the particle hygroscopicity is therefore the volume average of the three participating species:

$$\kappa_{\text{CCN}} = \sum_i x_i \kappa_i = x_{\text{org}} \kappa_{\text{org}} + x_{(\text{NH}_4)_2\text{SO}_4} \kappa_{(\text{NH}_4)_2\text{SO}_4} + x_{\text{NH}_4\text{NO}_3} \kappa_{\text{NH}_4\text{NO}_3}, \quad (1)$$

where x_i is the volume fraction of species i . The values of κ are 0.67 and 0.61 for $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 , respectively. The hygroscopicity of CCN (κ_{CCN}) can be derived from S^* :

$$\kappa_{\text{CCN}} = \frac{4A^3}{27D_p^3(S^*)^2}, \quad (2)$$

and the organic hygroscopicity κ_{org} is given by subtracting the contribution of the other species from the overall CCN hygroscopicity:

$$\kappa_{\text{org}} = \frac{1}{x_{\text{org}}} \left(\kappa_{\text{CCN}} - \kappa_{\text{NH}_4\text{NO}_3} x_{\text{NH}_4\text{NO}_3} - \kappa_{(\text{NH}_4)_2\text{SO}_4} x_{(\text{NH}_4)_2\text{SO}_4} \right), \quad (3)$$

The derivation of κ_{org} requires the volume fraction of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 of CCN at selected sizes, which were derived from size-resolved AMS measurements (particle time-of-flight “PToF” mode) as detailed below. AMS measurements were averaged over periods, during which chemical composition was essentially constant, to increase signal-to-noise ratios (SNR). Species volume fractions at each size were then derived from mass concentrations and densities of participating species. Based on the O:C and O:H atomic ratios during the periods, organics were assumed to have a density of 1250 kg m^{-3} (Kuwata et al., 2012). The volume fractions required to derive κ_{org} from Eq. (3) were then calculated by combining the volume concentrations of organics, sulfate, and nitrate. In this study, κ_{org} was derived based on hygroscopicity of CCN classified at five sizes ranging from 117 to 160 nm at which both the counting statistics of size-resolved CCN measurements (based on aerosol number) and the signal-to-noise ratio of the AMS measurements (aerosol mass based) were sufficient.

4.3 Uncertainty analysis for organic hygroscopicity derivation

Based on Eq. (2), the uncertainty in derived κ_{org} can be attributed to the uncertainties in κ_{CCN} and species volume fractions of CCN. The derivation of the uncertainty is detailed in Mei et al. (2013). As the contribution of BC to submicron aerosol mass is negligible, the uncertainty of derived κ_{org} is simplified to

$$\sigma_{\kappa_{\text{org}}}^2 = \left(\frac{\kappa_{\text{CCN}}}{x_{\text{org}}} \right)^2 \left(\frac{\sigma_{\kappa_{\text{CCN}}}}{\kappa_{\text{CCN}}} \right)^2 + (\kappa_{\text{inorg}} - \kappa_{\text{org}})^2 (1 - x_{\text{org}})^2 \left[\left(\frac{\sigma_{v_{\text{org}}}}{v_{\text{org}}} \right)^2 + \left(\frac{\sigma_{v_{\text{inorg}}}}{v_{\text{inorg}}} \right)^2 \right], \quad (4)$$

where v_i represents the volume concentration of species i , and κ_{inorg} is the average hygroscopicity of the particle inorganic component, which included $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 . For the derivation of the uncertainty in κ_{org} , a constant value of 0.64 was used for κ_{inorg} (Mei et al., 2013).

The first term on the right-hand side (RHS) of Eq. (4) is associated with the uncertainty in derived κ_{CCN} (i.e., $\frac{\sigma_{\kappa_{\text{CCN}}}}{\kappa_{\text{CCN}}}$), which is due to the accuracy of the dry size of particles classified by the DMA (Wang et al., 2003) and S^* derived from size-resolved CCN measurements. This uncertainty was estimated ranging from 5% to 12% (Mei et al., 2013). The second term on the RHS of Eq. (4) represents contributions due to the uncertainties in volume fractions of organics and inorganics (i.e., particle composition), derived from the mass concentrations measured by AMS and the densities of the species. For the purpose of estimating uncertainty in species volume fraction, an uncertainty of 10% was estimated for inorganic and organic volume concentrations, which were mainly due to the uncertainties in relative ionization efficiencies of AMS (Mei et al., 2013). Based on Eq. (4), both terms of the uncertainty decrease strongly with increasing x_{org} . Therefore, the derivation of κ_{org} was focused on periods with organic volume fraction higher than 60% (Mei et al., 2013).

5 Results

5.1 Hygroscopicity of activated particles

The hygroscopicity of size-selected CCN with diameter between 100 and 171 nm ranged from 0.10 to 0.2, with an average of 0.15, in agreement with the results derived from CCN measurements over Sacramento valley onboard NOAA WP-3D during California Nexus (CalNex; Moore et al., 2012). The hygroscopicity range was substantially lower than that proposed for continental sites (Andreae and Rosenfeld, 2008), likely due to the higher volume fraction of organics. The hygroscopicity of size-selected particles was averaged for sizes ranging from 100 to 171 nm, and its diurnal

variation is shown in Fig. 2a. Median and mean hygroscopicities were essentially the same, and both showed a very narrow range from 0.13 to 0.16. There was no significant diurnal trend in the statistics of κ_{CCN} , consistent with relatively constant organic volume fraction during the day (Fig. 1). Figure 2b shows the diurnal variation of E , which represents the fraction of classified particles that were CCN-active. Unlike earlier studies in the urban environment (i.e., near major aerosol sources), where E decreased to $\sim 70\%$ or lower during morning traffic hours (Lance et al., 2013; Padro et al., 2012; Mei et al., 2013), the E observed at the T1 site was greater than 90% essentially at all times, suggesting vast majority of particles within the 100–171 nm range were aged background particles. The average dispersion was 0.29, substantially lower than those observed in the urban environment (Su et al., 2010; Padro et al., 2012). The lower value of dispersion reflects more aged aerosols observed at the T1 site, and is consistent with the finding that aerosol composition becomes increasingly more homogeneous as particles age through coagulation and condensation of secondary species (Mei et al., 2013; Wang et al., 2010). The diurnal variation showed lower dispersion in later morning and afternoon, and is attributed to stronger SOA production during the period and subsequent condensation on existing particles.

5.2 Impact of organic hygroscopicity on calculated CCN concentration

The impact of κ_{org} on calculated CCN concentration (N_{CCN}) was examined using the following approach. CCN concentrations were calculated using four representative κ_{org} values, 0.03, 0.08, 0.13, and 0.18, which are within the typical range based on earlier laboratory studies (e.g., Prenni et al., 2007; Duplissy et al., 2008; Engelhart et al., 2008; Wex et al., 2009). Aerosol particles were assumed as internal mixtures, as suggested by the observed low hygroscopicity dispersion and close-to-unity E value for the size-selected particles. Based on this assumption, particle hygroscopicity was derived as the volume average of the following three species: $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 and organics. On average, the aerosol mass concentration measured by the AMS at the T1 site peaked around 200 nm (vacuum aerodynamic diameter, ~ 160 nm for mobility or volume average diameter assuming spherical particles), and minor variation in organic volume fraction was observed from 100 to 200 nm (vacuum aerodynamic diameter), which corresponds to a critical supersaturation range of $\sim 0.14\%$ to $\sim 0.4\%$. Therefore, for the purpose of examining the sensitivity of calculated N_{CCN} to κ_{org} , particle hygroscopicity was computed from the bulk composition (i.e., derived from AMS MS mode measurements) using Eq. (1). Based on the particle hygroscopicity and κ Köhler theory, the critical dry particle activation diameter (D_{pc}) was derived for the five supersaturations under which the total CCN concentrations were measured. The N_{CCN} at the five

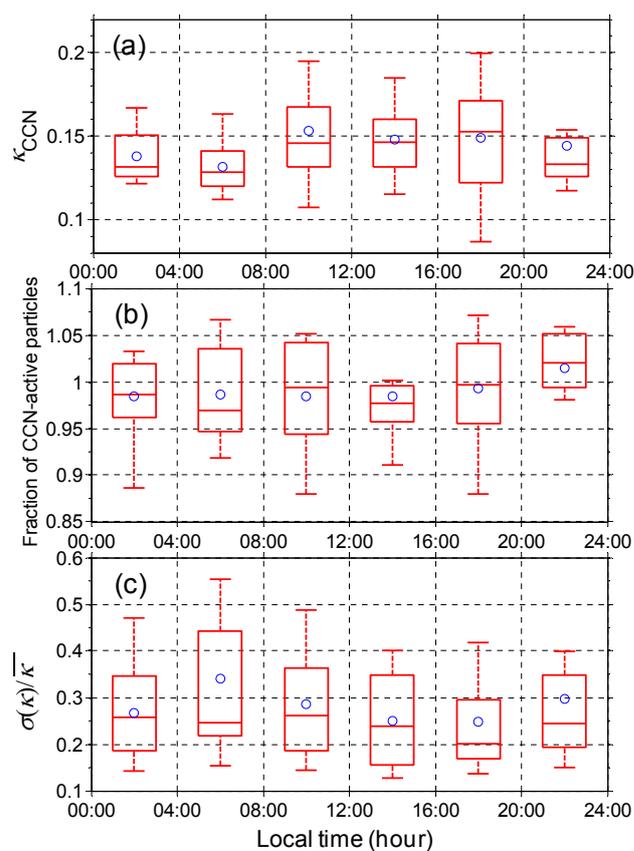


Fig. 2. The diurnal variations of (a) the average hygroscopicity, (b) maximum activation fraction, and (c) dispersion of size-selected CCN active particles ranging from 100 to 171 nm. The ends of the whiskers represent the minimum and maximum of data except for the outliers, which are defined as points outside of $\pm 2.7\sigma$. The bottom and the top of the box are the 25th and 75th percentiles, the line inside the box is the 50th percentile, and the blue circle represents the mean value.

supersaturations were then computed from D_{pc} and the measured dry particle size distributions.

The comparison of calculated N_{CCN} and that measured at three supersaturations, 0.12%, 0.23%, and 0.38%, are shown in Fig. 3 (comparison at the other two supersaturations are similar and not shown). When x_{org} was greater than 90%, calculated N_{CCN} was very sensitive to κ_{org} values, especially at lower supersaturations. The ratio of calculated to measured N_{CCN} , derived through a bivariate least squares fit (i.e., orthogonal distance regression), increased from 0.75 by almost 200% to 2.08 when κ_{org} increased from 0.03 to 0.18. Each incremental increase of 0.05 in κ_{org} , which is well within the range of organic hygroscopicity reported in literature, led to $\sim 40\text{--}50\%$ increase in the calculated N_{CCN} . At the higher supersaturation of 0.38%, the difference between N_{CCN} calculated using the different κ_{org} values reduced somewhat to about a factor 2 (i.e., ratio increased from 0.58 to 1.10), but was still very significant. This reduced

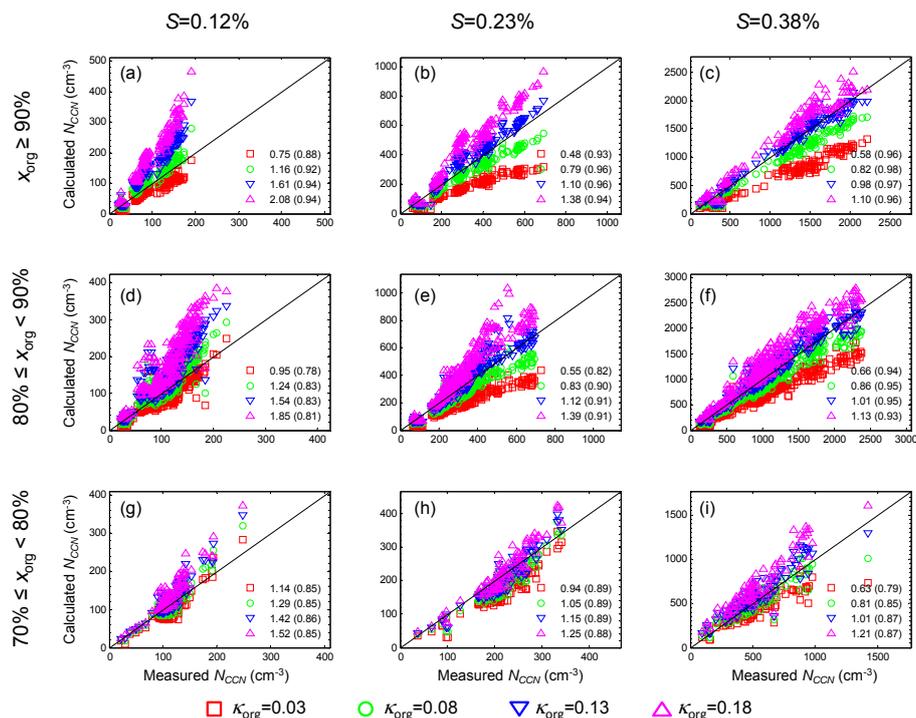


Fig. 3. Comparison of N_{CCN} calculated using four different κ_{org} values and the measurements at supersaturations of 0.12 % (a, d, g), 0.23 % (b, e, h), and 0.38 % (c, f, i) for cases when $x_{\text{org}} > 90\%$ (a, b, c), $80\% < x_{\text{org}} < 90\%$ (d, e, f), and $70\% < x_{\text{org}} < 80\%$ (g, h, and i). The slope (left, derived through a bivariate least squares fit) and the R^2 value (in the parenthesis) are shown for all assumed κ_{org} values in each plot. The solid black line corresponds to the 1 : 1 line.

sensitivity was due to the fact that a larger fraction of particle population was already CCN active at higher S . The sensitivity also strongly depended on the x_{org} . For example, when $80\% < x_{\text{org}} < 90\%$, N_{CCN} calculated at $S = 0.12\%$ increased by $\sim 100\%$ (i.e., ratio increased from 0.95 to 1.85) while κ_{org} increased from 0.03 to 0.18, compared to nearly a factor of 3 increase when x_{org} was greater than 90 %, and the increase was further reduced to $\sim 40\%$ (i.e., the ratio increased from 1.14 to 1.52) when $70\% < x_{\text{org}} < 80\%$. For most of the measurements, the κ_{org} value required for an agreement between calculated and measured N_{CCN} ranged from 0.03 to 0.15, in agreement with κ_{org} derived from size-resolved CCN measurements described below.

During CARES, aerosols observed at the T1 site were dominated by organics. For the comparison described above, 24 %, 54 %, and 16 % of the data points corresponded to $x_{\text{org}} > 90\%$, $80\% < x_{\text{org}} < 90\%$, and $70\% < x_{\text{org}} < 80\%$, respectively. Only 6 % of data points were associated with x_{org} less than 70 %. The decreasing sensitivity of the calculated N_{CCN} to κ_{org} is in agreement with earlier studies (e.g., Chang et al., 2007; Wang et al., 2008). When x_{org} is less than $\sim 60\%$, the overall hygroscopicity of internally mixed particles is dominated by inorganic species such as sulfate and nitrate, which have significantly higher κ values than organic compounds. As a result, the particle hygroscopic-

ity, and therefore the calculated CCN concentration, is relatively insensitive to κ_{org} . When x_{org} reaches 80 % or higher, the contribution of κ_{org} begins to dominate the overall particle hygroscopicity, and the value of κ_{org} strongly influences the calculated N_{CCN} . With stricter control of sulfur emission, aerosol organic fraction is likely to increase in the future. Therefore, simulated N_{CCN} will likely exhibit a stronger dependence on κ_{org} values when projecting future climate change. This again suggests the necessity of better understanding κ_{org} and its variation in the atmosphere for accurate prediction of N_{CCN} and aerosol indirect effects.

5.3 κ_{org} derived from measurements at CARE T1 site and comparison with previous studies

To increase SNR and reduce the uncertainty in derived κ_{org} , we averaged measurements over periods during which particle chemical composition essentially remained constant (i.e., the difference between the maximum and minimum of organic volume fraction was less than 10 %). A total of 18 such periods with average bulk organic volume fraction greater than 60 % were identified, and ranged from 7.6 to 14 h. These periods were approximately evenly distributed diurnally, and the total time was ~ 9 days, representing $\sim 50\%$ of the total sampling time. During these periods, E was greater than 96 %, and $\sigma(\kappa)/\bar{\kappa}$ was less than 0.3, indicating the

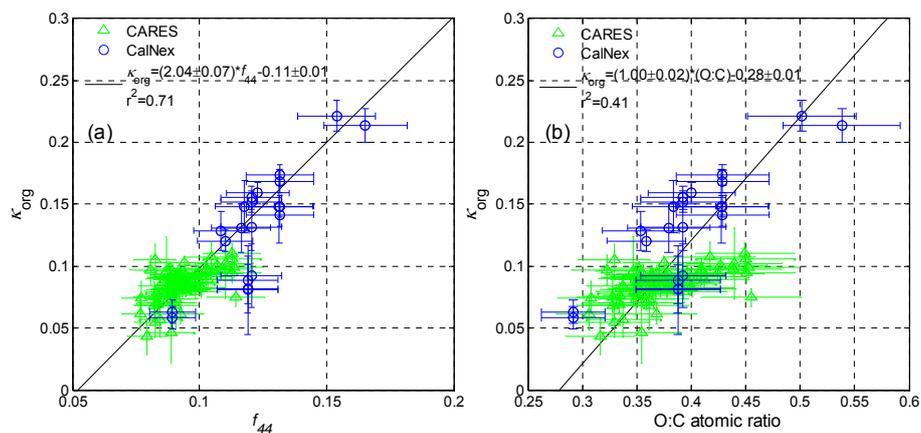


Fig. 4. Derived κ_{org} as a function of (a) f_{44} and (b) O : C atomic ratio and least squares fits.

assumption of internally mixed particles was mostly appropriate. As described earlier, for each period, the analysis focused on 5 sizes ranging from 117 nm to 160 nm. κ_{org} derived from these cases ranged from 0.04 to 0.11 with an average value of 0.08, within the ranges observed in earlier studies (e.g., Hersey et al., 2011). These values are also in agreement with results from earlier smog chamber studies, which showed the hygroscopicity ranged from 0.04 to 0.14 for secondary organic aerosol formed from both biogenic and anthropogenic VOC precursors (Duplissy et al., 2008; Engelhart et al., 2008; Prenni et al., 2007; Wex et al., 2009).

5.4 Relationship between κ_{org} and organic oxidation level

The relationship between derived κ_{org} and f_{44} , which is the fraction of total organic mass signal at m/z 44, is shown in Fig. 4a. The m/z 44 signal is due mostly to acids (Duplissy et al., 2011; Takegawa et al., 2007) or acid-derived species, such as esters, and f_{44} is closely related to the organic oxidation level (i.e., O : C ratio) (Aiken et al., 2008). The uncertainty of derived κ_{org} was calculated using the approach described earlier. The precision of f_{44} derived from measurements by the same AMS was estimated as 3 % (relative variation; Aiken et al., 2008), and the inter-instrument variability for f_{44} is about 10 % (relative variation; Ng et al., 2010). As the results are compared to earlier studies during which f_{44} was also derived from AMS measurements, the uncertainty in derived f_{44} was estimated as 10 % (Hayes et al., 2013). Also included in Fig. 4 are results based on similar analysis of the measurements carried out at the Los Angeles (LA) supersite during CalNex from 15 May to 4 June in 2010 (Mei et al., 2013). The LA supersite was principally a receptor site for pollution from downtown LA, and SOA was a major aerosol component at the site (Hayes et al., 2013). Overall, the dependences of κ_{org} on f_{44} are in agreement for organic aerosols observed at the CARES T1 and CalNex LA sites. Based on results from both sites, a least squares fit taking

into consideration uncertainties in both derived κ_{org} and f_{44} yielded $\kappa_{\text{org}} = 2.10(\pm 0.07) \times f_{44} - 0.11(\pm 0.01)$. The Pearson R^2 was 0.71, suggesting most of the variation in κ_{org} observed at the two sites can be explained by the variation in f_{44} alone.

The variation of κ_{org} was also examined as a function of organic oxidation level (i.e., O : C atomic ratio) as was done in earlier studies, and the result is shown in Fig. 4b. For both sites, O : C of size-selected CCN was calculated from size-resolved f_{44} using the specific relationship between O : C and f_{44} , which was characterized using the bulk O : C and f_{44} derived from MS mode data collected at each site. This is an adaptation of the technique described by Aiken et al. (2008), which assumes that the relationship between f_{44} and O : C is independent of particle size. As discussed in Setyan et al. (2012), two distinct oxygenated organic aerosol (OOA) factors were identified during this study, including a more-oxidized OOA ($f_{44} = 0.11$; O : C = 0.54) representative of biogenic SOA and a less-oxidized OOA ($f_{44} = 0.13$; O : C = 0.42) representative of SOA formed in photochemically processed urban emissions. These two OOA factors together accounted for almost all of the variances observed in O : C and f_{44} . As the two OOA factors exhibited similar size distributions (Setyan et al., 2012), they were likely internally mixed in particles during this study. Therefore, we expect the relationship between f_{44} and O : C was relatively independent of particle size.

The relationships were $\text{O : C} = 3.99 \times f_{44}$ and $\text{O : C} = 3.25 \times f_{44}$ for organic aerosols observed at the T1 site during CARES (i.e., this study) and the LA site during CalNex, respectively (Hayes et al., 2013; Setyan et al., 2012). The uncertainty in derived O : C was similarly estimated as 10 %. Whereas overall κ_{org} exhibited an increasing trend with increasing O : C, in agreement with earlier studies, the value of κ_{org} derived from this study was statistically lower than that derived from data collected at the CalNex LA site when O : C ranges from 0.35 to 0.45. A

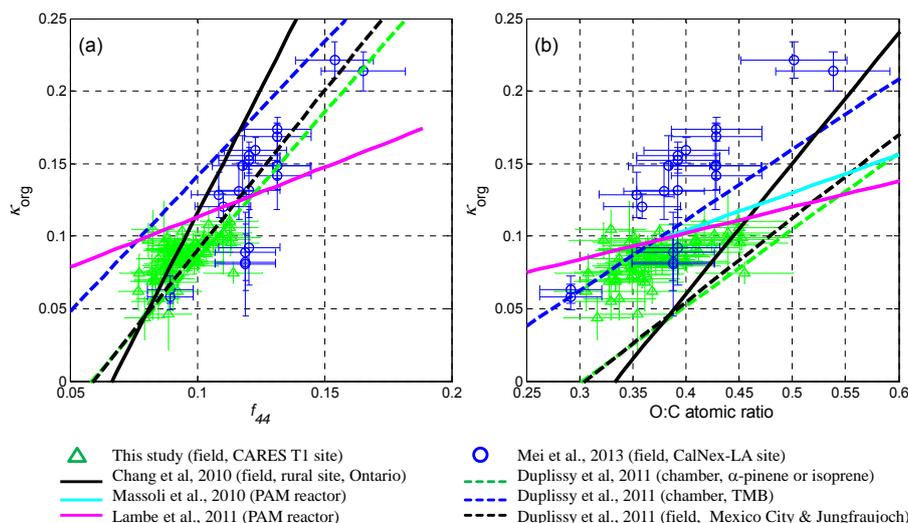


Fig. 5. Comparison with earlier studies on (a) the variation of κ_{org} with f_{44} and (b) the variation of κ_{org} with O:C. The solid and dashed lines represent κ_{org} derived under supersaturated and subsaturated conditions in earlier studies, respectively.

least squares fit of κ_{org} vs. O:C yielded $\kappa_{\text{org}} = 1.00(\pm 0.02) \times (\text{O}:\text{C}) - 0.28(\pm 0.01)$ with a significantly lower R^2 value of 0.41, suggesting that κ_{org} may be better parameterized by f_{44} than O:C.

The relationships between κ_{org} and f_{44} and between κ_{org} and O:C are compared to earlier studies described below (Fig. 5). Duplissy et al. (2011) reported κ_{org} (under subsaturated conditions) derived from the GF of SOA formed from 1,3,5-trimethylbenzene (TMB), a surrogate for anthropogenic precursors, and SOA formed from representative biogenic precursors including isoprene and α -pinene in a smog chamber. Also included in the comparison are the results derived from the GF of organic aerosols measured in Mexico City and at the high-alpine site Jungfraujoch, Switzerland (Duplissy et al., 2011). Chang et al. (2010) derived κ_{org} based on CCN measurements at a rural site in Ontario, Canada. Using size-resolved CCN measurements, Massoli et al. (2010) and Lambe et al. (2011) examined the hygroscopicity of SOA and oxidized POA (OPOA) formed from the oxidation of a range of precursors representing atmospherically relevant biogenic and anthropogenic sources. The SOA and OPOA particles were generated via controlled exposure of precursors to OH radicals and/or O_3 in a PAM flow reactor over timescales equivalent to 1–20 days of atmospheric aging resulting in O:C ratios ranging from 0.05 to 1.42.

The result from Massoli et al. (2010) was not included in Fig. 5a because f_{44} values were not available. Overall, results from different studies showed quite consistent relationships between κ_{org} and f_{44} . For example, the relationship derived from this study and the measurements at the CalNex LA site showed good agreement with those of ambient organic aerosols observed in Mexico City and at the high-alpine site

Jungfraujoch. At the same f_{44} , κ_{org} of SOA formed from TMB in a smog chamber was substantially higher than those of SOA formed from isoprene and α -pinene. One possible explanation is that for SOA formed from TMB photooxidation, the acids present in the aerosol are mainly mono-acids, while the acids found in the SOA from α -pinene or isoprene photooxidation are approximately half mono- and half di-acids (Duplissy et al., 2011). At a given f_{44} value, κ_{org} of ambient organic aerosol observed at the CARES T1 site, CalNex LA site, Mexico City, and Jungfraujoch was mostly between those of SOA formed from TMB and α -pinene or isoprene in the smog chamber, possibly because ambient SOA was formed from both anthropogenic and biogenic precursors. Chang et al. (2010) reported similar κ_{org} values at low f_{44} around 0.08–0.10, but a steeper increase of κ_{org} with increasing f_{44} than those observed in this study and at the CalNex LA site. Because κ_{org} was derived from total CCN measurement (i.e., not size-resolved) in Chang et al. (2010), the relatively large uncertainty may partially explain some of the differences. For OA generated in PAM reactors, κ_{org} overlapped with those derived from field measurements when f_{44} ranges from 0.12 to 0.14, but exhibited a substantially weaker dependence on f_{44} .

All studies show that κ_{org} generally increases with increasing O:C. However, compared to the relationship between κ_{org} and f_{44} , the relationship between κ_{org} and O:C exhibits more significant differences among the studies. For example, at O:C ratio of 0.5, κ_{org} derived in above studies ranged from ~ 0.1 to ~ 0.2 . For the results from Duplissy et al. (2011) and Chang et al. (2010), the differences may be partially due to the uncertainty in derived O:C values. At present, AMS data analysis software only allows derivation of bulk O:C through analysis of high-resolution mass spectral obtained

during the MS mode operation. This approach was employed by Massoli et al. (2010) and Lambe et al. (2011) to derive the bulk O : C, which should represent O : C at various CCN sizes in their studies, because no substantial O : C dependence on particle size is expected for organic aerosols formed in the PAM reactor. For this study and Mei et al. (2013), organic O : C at measured CCN sizes was derived from size-resolved f_{44} using the relationship between O : C and f_{44} , which was characterized using the bulk O : C and f_{44} derived from MS mode data collected at each site. This approach was also employed to derive O : C from f_{44} for some of the results presented in Lambe et al. (2011). Therefore, we expect that O : C values derived in this study, Lambe et al. (2011), and Mei et al. (2013) are reasonably accurate. Chang et al. (2010) and Duplissy et al. (2011) derived O : C using the relationship between O : C and f_{44} reported in an earlier study (Aiken et al., 2008), which might not be completely accurate for the aerosols observed in their studies.

Similar to the relationship between κ_{org} and f_{44} , κ_{org} of OA generated in a PAM reactor (Massoli et al., 2010; Lambe et al., 2011) exhibited a weaker dependence on O : C than those derived from this study and Mei et al. (2013). At O : C values greater than 0.5, κ_{org} reported by Massoli et al. (2010) and Lambe et al. (2011) were substantially lower than those derived from field measurements (Mei et al., 2013). The organic mass loading examined by Massoli et al. (2010) ranged from 1 to 100 $\mu\text{g m}^{-3}$, which encompasses the typical range of ambient OA mass loading. In addition, the relationship between κ_{org} and O : C reported by Massoli et al. (2010) exhibited little dependence on organic mass loading. Therefore the differences in the relationship between κ_{org} and O : C among the studies could not be explained by the variations in organic mass loading, and may be due to the differences in organic composition between ambient organic aerosols and those formed in PAM reactors. For example, the formation of SOA proceeded in the absence of NO_x inside a PAM reactor in Massoli et al. (2010) and Lambe et al. (2011). However, ambient SOA may form under different NO_x conditions, especially in the urban environment (e.g., at the CalNex LA site). In addition, the concentrations of oxidants inside a PAM reactor are several orders of magnitude higher than typically observed in the ambient atmosphere, which may potentially lead to different compounds in the SOA formed. Cloud processing and aqueous chemistry in wet aerosols may also contribute substantially to SOA formation, while SOA are mainly formed through gas phase reactions in a smog chamber or PAM reactor. This may also lead to different SOA composition and therefore the relationship between κ_{org} and O : C. However, it is worth noting that the relationship between κ_{org} and f_{44} for SOA formed in a smog chamber (Duplissy et al., 2011) is quite consistent with that derived from some of the field studies (Fig. 5a). These discrepancies suggest that more results on κ_{org} of ambient aerosols are needed to better understand and represent organic hygroscopicity in climate models, and future studies are needed to verify and

understand the differences in κ_{org} between ambient OA and those formed in PAM reactors shown in Fig. 5.

Organic aerosols exhibit a range of relationships between f_{44} and O : C, as evidenced by the differences among the relationships observed at the T1 site, the CalNex LA site (Hayes et al., 2013), and those reported in previous studies (e.g., Aiken et al., 2008). The more consistent relationships between κ_{org} and f_{44} derived in different studies (Fig. 5a) and the higher R^2 value for the linear regression of κ_{org} on f_{44} (Fig. 4a) suggest that κ_{org} may be better parameterized using f_{44} than O : C. The stronger correlation between κ_{org} and f_{44} could be due to the following reasons. One key determinant of the hygroscopicity of organic compound is its water solubility. For typical ambient particles that are mixtures of both organic and inorganic species, organics with solubility less than $\sim 5 \times 10^{-4}$ have negligible contribution to CCN activation (i.e., negligible contribution to derived κ_{org}), whereas organics with solubility greater than ~ 0.05 are completely dissolved at the point of activation (Petters and Kreidenweis, 2008). Here the solubility is defined as the volume of solute per unit volume of water present in a saturated solution. The CO_2^+ (m/z 44) is due mostly to acids (Duplissy et al., 2011) or acid-derived species, such as esters. Organic acids typically have higher solubility in water, and therefore may contribute significantly to the overall κ_{org} . Other oxygenated compounds in organic aerosol such as aldehydes may have much lower solubility, and therefore negligible contribution to the derived κ_{org} if their solubility is less than $\sim 5 \times 10^{-4}$. This may explain the stronger correlation between κ_{org} and f_{44} , as f_{44} is closely related to the fraction of organic acids. It is worth noting that non-acid compounds such as methyl tetrols identified in SOA formed from isoprene also have high water solubility. However, these compounds may contribute to only a small fraction of the total organic aerosols, especially for those formed under high NO_x condition (e.g., Edney et al., 2005). Currently, the identity and the solubility of many organic compounds in atmospheric aerosols are not known, and data on κ_{org} for ambient aerosol are still quite limited. Future measurements are needed to verify the above findings, and to improve our understanding of κ_{org} and its relationship to composition.

6 Conclusions

During the CARES campaign, activation fraction of size-resolved aerosol particles and aerosol chemical composition were characterized at the T1 site (~ 60 km downwind of Sacramento, California) from 10 June to 28 June 2010. Increases in aerosol mode diameter and organic mass loading were observed from 12:00 to 18:00, and are attributed to advection of secondary organic aerosols formed in the Sacramento urban plume through photochemical reactions. The hygroscopicity of CCN-active particles with diameter from 100 to 170 nm, derived from the size-resolved activated

fraction, ranged from 0.10 to 0.20, with an average of 0.15, which is substantially lower than that proposed for continental sites (Andreae and Rosenfeld, 2008). The low κ_{CCN} value was due to the high organic volume fraction, averaged over 80% at the T1 site. The derived κ_{CCN} exhibited little diurnal variation, consistent with the relatively constant organic volume fraction observed. Unlikely earlier studies in the urban environment where E decreased to $\sim 70\%$ or lower during morning traffic hours, E was always greater than $\sim 90\%$ for particles with diameter between 100 and 171 nm, suggesting the vast majority particles within this size range were aged background particles. The average hygroscopicity dispersion of size-selected CCN was 0.29, substantially lower than those observed in the urban environment (Su et al., 2010; Padro et al., 2012; Mei et al., 2013), also reflecting more aged aerosols observed at the T1 site. These observations are in agreement with previous studies that show that hydrophobic particles emitted in urban areas quickly become internal mixtures and hydrophilic by condensation of secondary hygroscopic species, such as SOA (Riemer et al., 2004, 2009; Moffet and Prather, 2009; Wang et al., 2010; Mei et al., 2013), and aerosol composition becomes increasingly more homogeneous as particles age through coagulation and condensation of secondary species (Mei et al., 2013; Wang et al., 2010).

The sensitivity of calculated N_{CCN} to κ_{org} was examined for aerosol observed at the T1 site. The sensitivity increased with increasing organic volume fraction, in agreement with earlier studies (e.g., Chang et al., 2007; Wang et al., 2008). Due to the large organic volume fraction, κ_{org} strongly impacted calculated N_{CCN} . For the vast majority of the cases, an increase of κ_{org} from 0.03 to 0.18, which are within the type range, doubled the calculated N_{CCN} . Even a minor increase of κ_{org} from 0.08 to 0.13 led to a 30% increase of the calculated N_{CCN} . Future stricter control of sulfur emission will likely lead to increased aerosol organic volume fraction and therefore stronger dependence of simulated N_{CCN} to κ_{org} when projecting future climate change.

Organic hygroscopicity was derived from κ_{CCN} and aerosol chemical composition, and its variations with f_{44} and O:C were compared to results from previous studies. Overall, the relationships between κ_{org} and f_{44} are quite consistent for ambient OA and those formed in a smog chamber. However, κ_{org} of OA formed in PAM reactors exhibited weaker dependence on f_{44} or O:C when compared to those of ambient OA. The discrepancy may be due to the differences in organic compositions. Compared to the relationship between κ_{org} and f_{44} , the relationship between κ_{org} and O:C exhibits more significant differences among different studies. While some of the differences may be due to the uncertainty in derived O:C values, the comparison suggests κ_{org} may be better parameterized using f_{44} . A least squares fit of κ_{org} on f_{44} yielded $\kappa_{\text{org}} = 2.04(\pm 0.07) \times f_{44} - 0.11(\pm 0.01)$ with a Pearson R^2 value of 0.71. One possible explanation for the stronger correlation between κ_{org} and f_{44} is that the signal at

m/z 44 is closely related to organic acids, which may dominate the overall κ_{org} due to its relatively high water solubility and hygroscopicity. Future measurements of κ_{org} of ambient aerosols are needed to verify these findings, and to better understand κ_{org} and its relationship to the composition for their representations in climate models.

Supplementary material related to this article is available online at <http://www.atmos-chem-phys.net/13/12155/2013/acp-13-12155-2013-supplement.pdf>.

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