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Oxidation of ambient biogenic secondary organic aerosol by hydroxyl radicals: Effects on cloud condensation nuclei activity

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[1] Changes in the hygroscopicity of ambient biogenic secondary organic aerosols (SOA) due to controlled OH oxidation were investigated at a remote forested site at Whistler Mountain, British Columbia during July of 2010. Coupled photo-oxidation and cloud condensation nuclei (CCN) experiments were conducted on: i) ambient particles exposed to high levels of gas-phase OH, and ii) the water-soluble fraction of ambient particles oxidized by aqueous-phase OH. An Aerodyne Aerosol Mass Spectrometer (AMS) monitored the changes in the chemical composition and degree of oxidation (O:C ratio) of the organic component of ambient aerosol due to OH oxidation. The CCN activity of size-selected particles was measured to determine the hygroscopicity parameter ($\kappa_{\text{org,CCN}}$) for particles of various degrees of oxygenation. In both cases, the CCN activity of the oxidized material was higher than that of the ambient particles. In general, $\kappa_{\text{org,CCN}}$ of the aerosol increases with its O:C ratio, in agreement with previous laboratory measurements.

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1. Introduction

[2] One of the largest uncertainties in global radiative forcing assessment is the cooling effect of atmospheric particulates via their ability to act as CCN, which is dependent on their size and composition. Organic compounds constitute a large fraction of ambient aerosol, as demonstrated at various locations in the Northern Hemisphere [Zhang *et al.*, 2007]. Characterization of organic aerosol hygroscopicity is thus crucial for reducing uncertainties in current climate models.

[3] The earliest studies of organic aerosol CCN properties used model compounds, mainly chosen by their solubility properties [Cruz and Pandis, 1997; Corrigan and Novakov, 1999; Pradeep Kumar *et al.*, 2003; Shantz *et al.*, 2003]. These studies illustrated that highly water soluble compounds

give rise to good CCN – indicating that organic constituents could be of comparable importance to cloud droplet formation as highly soluble, inorganic components. CCN closure studies were also performed [e.g., VanReken *et al.*, 2003; Chang *et al.*, 2007]. Recent lab work has demonstrated that SOA, formed by photo-oxidation processes from specific precursors, is quite hygroscopic [Huff Hartz *et al.*, 2005; VanReken *et al.*, 2005; King *et al.*, 2007; Prenni *et al.*, 2007; Duplissy *et al.*, 2008; Engelhart *et al.*, 2008; Massoli *et al.*, 2010; Lambe *et al.*, 2011b].

[4] Given that a complete chemical characterization of ambient particles is not yet achievable, their CCN properties cannot be calculated from first-principles. As a result, the particle hygroscopicity is now typically described using the κ -Köhler method, where one parameter (κ) describes the average properties (e.g., molecular weight and solubility) of all compounds present [Petters and Kreidenweis, 2007]. This eliminates the need for the specific chemical identities of the constituents found in ambient aerosol and allows for a simple representation of CCN activation in global climate models.

[5] In this context, a highly oxygenated organic particle is more likely to be a better CCN due to the increased polarity and solubility of its constituents. Given that oxidative aging leads to more functionalized solute molecules [George and Abbatt, 2010a], it is reasonable to inquire whether such aging increases the hygroscopicity of these particles. For laboratory data, a simple trend of increasing CCN activity and sub-saturated hygroscopicity with degree of SOA oxidation (approximated by O:C atomic ratios) has been reported [Jimenez *et al.*, 2009; Massoli *et al.*, 2010; Duplissy *et al.*, 2008, 2011]. However, since the chemical composition of laboratory SOA is different than that measured in the atmosphere [Hallquist *et al.*, 2009], it is necessary to determine how oxidation processes affect the CCN activation of ambient SOA. In particular, Chang *et al.* [2010] conducted a CCN closure study using ambient aerosol measurements, where a direct relationship between the organic aerosol's degree of oxygenation and its hygroscopicity parameter determined from CCN activity ($\kappa_{\text{org,CCN}}$) was proposed. An objective of the current study was to investigate the postulate made by Chang *et al.* [2010] that there is a simple linear relationship between $\kappa_{\text{org,CCN}}$ of an organic aerosol and its degree of oxidation.

[6] Here we report the degree to which OH-initiated gas- and aqueous-phase oxidation affect the CCN activity of ambient organic aerosol sampled in a biogenically-rich region. This marks the first deployment of a portable flow tube apparatus that can generate controlled levels of gas-phase OH, and it demonstrates the relationship between the CCN activity of ambient particles and their O:C ratios due to

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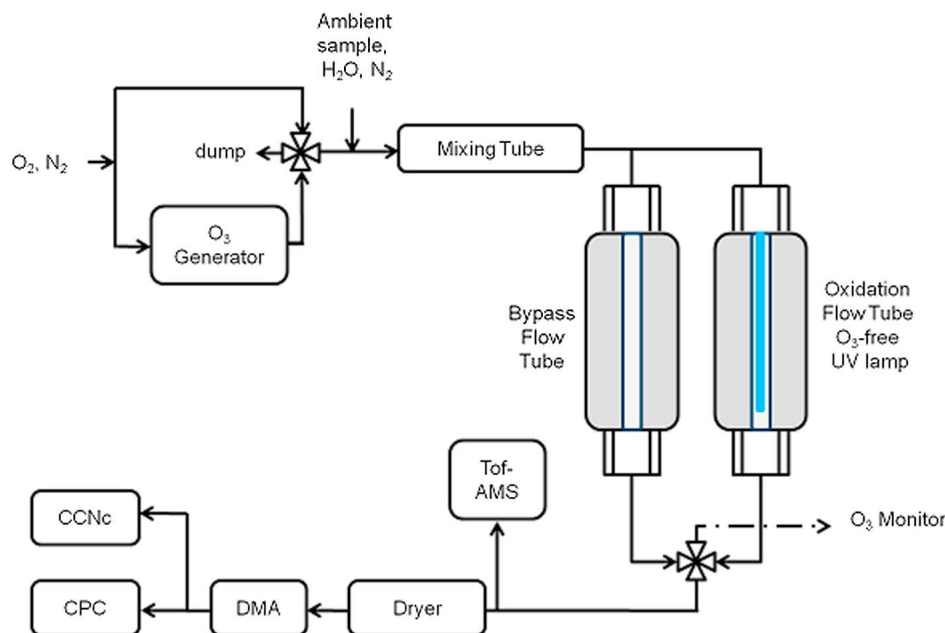


Figure 1. Toronto Photo-Oxidation Tube (TPOT) setup for the study of the gas-phase OH oxidation of ambient organic aerosol and their CCN activity.

OH oxidation. The study of ambient particles, in which their O:C ratios were changed by OH exposure on-site, further supports the observations from earlier laboratory experiments [Jimenez *et al.*, 2009; Massoli *et al.*, 2010; George and Abbatt, 2010b; Duplissy *et al.*, 2011; Lambe *et al.*, 2011a] of increasing CCN activity with oxidation, and the relationship of $\kappa_{\text{org,CCN}}$ vs. O:C postulated by Chang *et al.* [2010] and Lambe *et al.* [2011b].

2. Experiment

[7] Experiments were conducted at the Raven's Nest site at Whistler, BC, Canada (1300 m ASL, 50°N 122°W) as part of Environment Canada's Whistler Aerosol and Cloud Study (WACS) 2010. The site is situated in a coniferous forest that produces high levels of biogenic organic aerosol [Schwartz *et al.*, 2010] during warm summertime conditions, with minimal contributions from local pollution and no evidence for biomass burning impact during the periods described below that had daytime temperatures ranging from 20 to 27°C.

2.1. Gas-Phase OH Oxidation

[8] Gas-phase OH oxidation of ambient particles was conducted in the Toronto Photo-Oxidation Tube (TPOT) (Figure 1), which is a modified version of a system [George *et al.*, 2007; Lambe *et al.*, 2011b] that produces high OH exposures ($1.0\text{--}1.3 \times 10^{12}$ molecules cm^{-3} s) via the photolysis ($\lambda = 254$ nm) of gas-phase O_3 ($1.3\text{--}2.7 \times 10^{13}$ molecules cm^{-3}) in the presence of water vapour (relative humidity = 40%) for a residence time of 2.2 minutes in the oxidation region. Modifications from the technique described in previous publications [George *et al.*, 2007; Lambe *et al.*, 2011b] include the use of a wider diameter, stainless steel flow reactor that was electrochemically coated with amorphous

silicon material (SilcoTek Corp.) to reduce gas-phase adsorption and the use of multiple point aerosol injection to accelerate the mixing of particles with the gas flows. The sample (1100 sccm) was introduced through 3 m of electrochemically coated 6 mm o.d. stainless steel tubing (no cyclone) that extended 0.5 m above the roof of the sampling site. The UV lamp was placed in the centre of the flow tube, and was surrounded by a quartz tube cooled with a flow of room air (~ 20 lpm). The OH concentration was determined by monitoring the decay of methyl-ethyl-ketone by reaction with OH using the Ionicon PTR-MS. The OH exposures were equivalent to 8–10 days (24-h) of ambient OH exposure of 1.5×10^6 molecules cm^{-3} .

[9] During normal operation, ambient aerosol was sampled continuously. Aerosol is mixed with a humidified flow (700 sccm). An automated switching valve alternately injects either an ozone-containing flow (200 sccm) or a blank flow of O_2 and N_2 (200 sccm) with a period of 12 min. These flows are allowed to mix and then pass into the reaction tube, where they are irradiated with UV light. If the ambient aerosol was mixed with ozone, OH radicals are produced; otherwise unreacted particles are measured. In addition to reaction with OH, ambient aerosol can potentially react with ozone and/or be volatilized by heat and UV light produced from the lamp. Ozone control experiments were conducted by comparing organic mass concentrations and mass spectra with and without added ozone under dark conditions using a bypass tube. No reaction with ozone was observed. Volatilization control experiments were conducted by comparing ozone-free organic AMS mass spectra and concentrations in light (i.e., UV lamp on) vs. dark conditions. With the lamp on, the temperature increased by approximately 4°C (25°C to 29°C). In the presence of UV light, an 18% decrease in total organic mass was observed, which can be due to both increased temperature and photolysis of aerosol compounds leading to

their volatilization. More details on these control experiments are in the auxiliary material.¹ Ambient particles were subjected to OH and no OH oxidation alternatively for 12 minutes each, for the total time period required to complete a CCN activation curve scan (described below). Three time periods from each of two days of experiments are analyzed here.

2.2. Aqueous-Phase OH Oxidation

[10] A sampling inlet for particle filter samples was situated beside that for the gas-phase OH oxidation studies. The particle samples passed through a cyclone with PM1 cut size (UGR, Model 463) and were collected on 47 mm Teflon filters (2.0 μm pores) for 24 hour periods, following which water extraction was conducted. The aqueous solutions were oxidized on-site using our custom photoreactor [Lee *et al.*, 2011], with a final H_2O_2 concentration of 70 mM (continuously stirred) and then irradiated by a UV lamp (UVP, 254 nm) inserted into the solution. The solutions were oxidized for 10 minutes, then nebulized (TSI 3076 atomizer) with compressed air for the detection by particle instruments. Solutions without H_2O_2 were also nebulized under dark conditions (i.e., UV lamp off). Four samples are considered for the current analysis.

2.3. Particle Composition and CCN Measurements

[11] The non-refractory particle composition was measured by an Aerodyne Time-of-Flight aerosol mass spectrometer (C-ToF-AMS). For the CCN measurements, particles were first dried using a silica gel diffusion dryer and then size-selected at a mobility diameter of 75 nm (TPOT output) or 100 nm (aqueous reactor output) by a TSI-3081 DMA before being measured by the CCNC. The CCN active number fraction was determined from the ratio of the number of CCN-active particles measured by one channel of a DMT-200 CCN counter to the total particle number concentration, measured by a TSI-3010 Condensation Particle Counter (CPC).

[12] To obtain a CCN activation curve, multiple supersaturations between 0.07–1.0% were scanned for a period of 24 minutes on each supersaturation for the gas-phase oxidation experiments, and 10 minutes for the aqueous-phase oxidation. CCN activation curves were constructed by calculating the fraction of activated particles, determined from the CCN/CPC ratio at the various supersaturation values. Using the dry mobility diameter (D_i), and the critical supersaturation (Sc), defined as the supersaturation in which 50% of the size-selected particles act as CCN, the kappa-parameter for the total particles was calculated as described by *Petters and Kreidenweis* [2007],

$$Sc = \frac{D^3 - D_i^3}{D^3 - D_i^3(1 - \kappa_{\text{total,CCN}})} \exp\left(\frac{4\sigma_w M_w}{RT\rho_w D}\right) \quad (1)$$

where D is the droplet wet diameter, M_w , ρ_w and σ_w are the molecular weight, density, and surface tension of water.

[13] The overall κ of the particles ($\kappa_{\text{total,CCN}}$) is calculated as the sum of the volume-fraction weighted average κ_{CCN} 's of the individual components. To arrive at the

kappa-parameter for the organic component of the particles, the following equation was used [Petters and Kreidenweis, 2007]:

$$\kappa_{\text{total,CCN}} = \varepsilon_{\text{org}}\kappa_{\text{org,CCN}} + \varepsilon_{\text{inorg}}\kappa_{\text{inorg,CCN}} \quad (2)$$

where ε_{org} is the volume fraction of the organic component determined from the C-ToF AMS, assuming an initial organic density of 1200 kg m^{-3} . Only samples with $\varepsilon_{\text{org}} \geq 67\%$ (AMS mass fraction, $f_{\text{Org}} \geq 0.63$) are considered for the current analysis, so that the changes in $\kappa_{\text{org,CCN}}$ due to oxidation are statistically significant and not dominated by the inorganic fraction. For example, the estimated uncertainty in $\kappa_{\text{org,CCN}}$ is 25% when $\varepsilon_{\text{org}} = 0.8$, with smaller values for larger ε_{org} values. For the gas-phase oxidation experiments, the increase in the organic component density due to oxidation was accounted for, using results obtained from *George and Abbatt* [2010b] where they determined changes in ρ_{org} of laboratory α -pinene SOA as a function of OH exposure. This amounts to a relative change in the $\kappa_{\text{org,CCN}}$ of only 0.5% for the current analysis. For the aqueous oxidation experiments, changes in organic density were not corrected for since the OH exposures used were unknown. The aerosol inorganics measured by the AMS were considered in the calculation as ammonium nitrate ($\kappa = 0.72$, density = 1730 kg m^{-3}) and ammonium sulfate ($\kappa = 0.59$, density = 1770 kg m^{-3}) [Windholz, 1983; Clegg *et al.*, 1996, 1998; Wexler and Clegg, 2002]. During the periods studied, ammonium sulfate accounted for more than 80% of the measured inorganic mass. At times the particle was not fully neutralized but the sensitivity of calculated $\kappa_{\text{org,CCN}}$ to particle acidity was shown to be very low. An assumption made in the analysis was that all particles were internally mixed. Molecular O:C ratios were estimated from the fraction of the total organic signal measured at m/z 44 (f44), using the empirical relationship formulated by *Aiken et al.* [2008]. The AMS measurements were averaged over the period of time required to complete the corresponding CCN activation scans.

3. Results and Discussion

[14] Sample CCN activation curves from both gas- and aqueous-phase OH oxidation experiments are shown in Figure 2. For all experiments, the critical supersaturation (Sc) decreased for samples subjected to oxidation, compared to the control samples. The average $\kappa_{\text{org,CCN}}$ values for the TPOT experiments were smaller than those for the aqueous-phase samples as there may be some larger, less soluble organic species in the ambient particles compared to the water-soluble component. The CCN activation curves for particles subjected to aqueous-phase OH oxidation are steeper compared to those from gas-phase OH oxidation for two reasons. First, the aqueous reactor is expected to produce more uniform OH exposures as the solution was constantly stirred. Second, the extraction and dissolution process is likely to homogenize the samples.

[15] For all the experiments considered, the O:C ratios increased after oxidation (see auxiliary material for detailed results on all experiments, including sample aerosol mass spectra). The mass fraction of m/z 44 (predominantly CO_2^+) to the total organic component (f44), an indicator of highly oxidized species, increased while the mass fraction of m/z 43 (predominantly $\text{C}_2\text{H}_3\text{O}^+$) to the total organic component

¹Auxiliary materials are available in the HTML. doi:10.1029/2011GL049351.

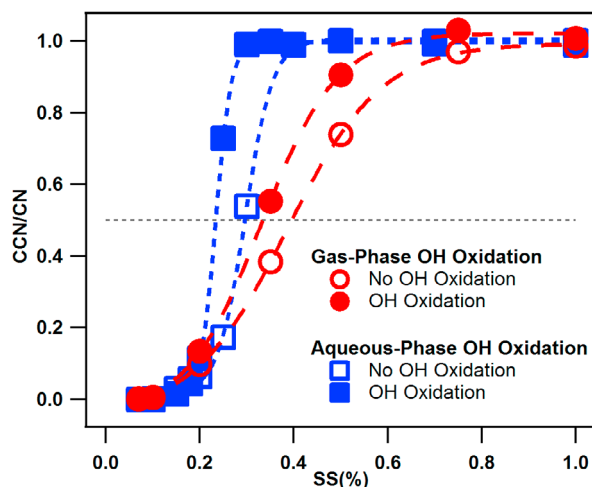


Figure 2. Activated particle fraction (CCN/CN) plotted as a function of the water supersaturation (SS) for unoxidized and oxidized ambient particles by gas-phase OH oxidation ($d_m = 75$ nm; July 22, 2010, 00:02–02:50) (red circle) and aqueous-phase OH oxidation ($d_m = 100$ nm; July 8, 2010) (blue square).

(f43), an indicator of less oxidized species, decreased slightly [Ng *et al.*, 2011]. For the gas-phase OH oxidation experiments, the changes in hygroscopicity can arise from conversion of insoluble organic species to more soluble species, changes in the properties of dissolved constituents, the loss of volatile components that are less hygroscopic, and the condensation of oxidation products onto the aerosol. While it is possible there was some condensation of oxidation products, an average decrease in the total organic mass of 10% was observed and so changes in hygroscopicity due to this process were likely to be minor. Note that the small increase in the mass fraction of sulphate to total particle mass (fSO_4^{2-}) due to oxidation are not large enough to explain the overall increase in $\kappa_{total,CCN}$ observed.

[16] Figure 3 shows the relationship between O:C to $\kappa_{org,CCN}$. Literature values of other oxidation–CCN measurements, mostly from lab studies, are included for comparison. We note that other studies have examined this relationship through the hygroscopic growth factor ($HGF_{95\%}$) [Jimenez *et al.*, 2009; Massoli *et al.*, 2010; Duplissy *et al.*, 2011]. The $\kappa_{org,CCN}$ and O:C values from a laboratory oxidative study of O_3 - α -pinene SOA are included; specifically, the “lamp” and “OH” flow tube conditions from Figure 9a of

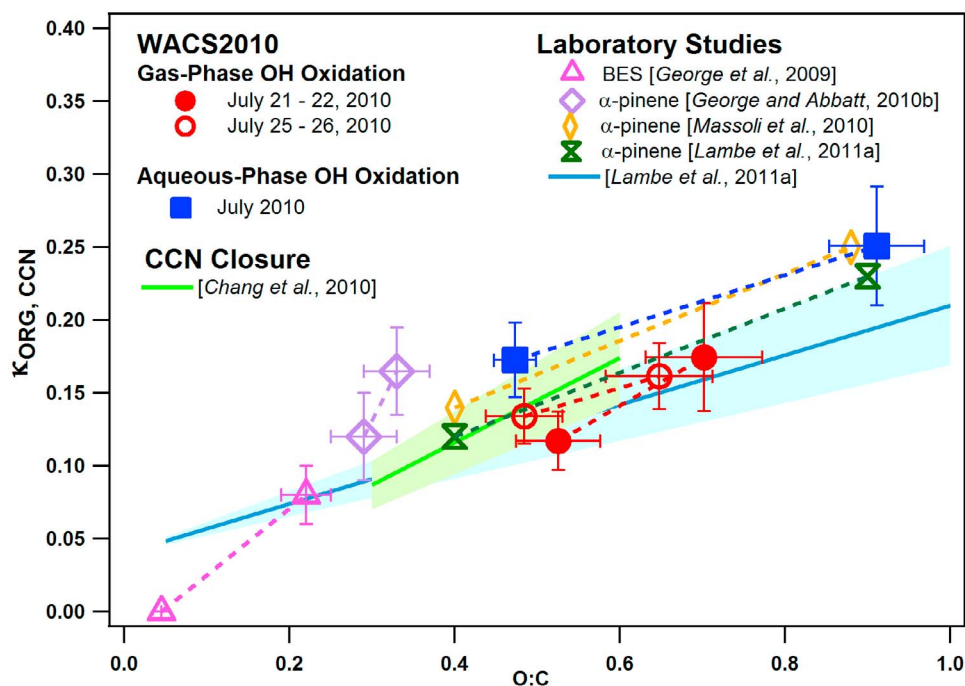


Figure 3. Relationship between O:C and $\kappa_{org,CCN}$ from the current study and from several laboratory studies of model POA and biogenic SOA [George *et al.*, 2009; George and Abbatt, 2010b; Massoli *et al.*, 2010; Lambe *et al.*, 2011a], and a field CCN closure study [Chang *et al.*, 2010] for comparison. The Lambe *et al.* [2011a] solid line represents a fit for SOA from a number of precursors. For each pair of points, the samples of the lowest and highest O:C values are shown from each study. Dashed lines are included only to indicate the relationship between these two points. The following were the OH exposures used for the laboratory studies of: BES (3.0×10^{12} molecules cm^{-3} s) [George *et al.*, 2009], O_3 - α -pinene SOA (1.3×10^{12} molecules cm^{-3} s) [George and Abbatt, 2010b], OH- α -pinene SOA (1.2×10^{12} molecules cm^{-3} s) [Massoli *et al.*, 2010] and OH- α -pinene SOA (1.7×10^{12} molecules cm^{-3} s) [Lambe *et al.*, 2011a]. The shaded region illustrates the uncertainty of the $\kappa_{org,CCN}$ and O:C relationships derived from the CCN closure study [Chang *et al.*, 2010] and laboratory generated organic aerosol [Lambe *et al.*, 2011a]. The uncertainties in the calculated values of O:C and $\kappa_{org,CCN}$ are mainly influenced by the systematic errors associated with each measurement, as discussed in the main text. Also, daily averages are shown for the gas-phase OH oxidation experiments, and the average of 4 one-day aqueous-phase OH oxidation experiments (results from individual experiments included in the auxiliary material).

George and Abbatt [2010b] provided the best comparison of experimental conditions to the no OH and OH oxidation conditions employed in this study. The $\kappa_{\text{org,CCN}}$ values from oxidation of bis-2-ethylhexyl sebacate (BES) were also included as a model of primary organic aerosol [George *et al.*, 2009], although we recognize that this is a different starting material from the monoterpene. The corresponding O:C ratios for BES were calculated from the measured f44 values, using the relationship in Figure A1 from Lambe *et al.* [2011b]. Results from other lab CCN studies of α -pinene SOA are included to further evaluate the generality of the relationship of $\kappa_{\text{org,CCN}}$ and O:C [Massoli *et al.*, 2010; Lambe *et al.*, 2011a]. Also included in the plot are two relationships between $\kappa_{\text{org,CCN}}$ and O:C, i.e., from Chang *et al.* [2010], which was derived from CCN closure at a rural field site under the postulate of a direct linear relationship between the two quantities (solid green line), and from Lambe *et al.* [2011b], which was derived from various laboratory generated organic aerosol (solid blue line).

[17] The uncertainties in the calculated values of O:C and $\kappa_{\text{org,CCN}}$ are mainly influenced by the systematic errors associated with each measurement, including the aerosol's chemical composition (AMS) [Bahreini *et al.*, 2009], instrument supersaturation (CCNC), particle size selection (DMA), and aerosol number (CPC). The uncertainties reported for the empirical relationship formulated by Aiken *et al.* [2008] to calculate O:C ratios from f44 were also considered. For this study, the average uncertainty was estimated to be 15% for $\kappa_{\text{org,CCN}}$ and 10% for O:C ratios. The results obtained from the gas- and aqueous-phase OH oxidation of ambient organic aerosol follow a direct positive relationship between O:C and $\kappa_{\text{org,CCN}}$, as observed in previous lab studies. Also, the CCN closure result from Chang *et al.* [2010] is consistent with the other measurements. Given the range of potential organic aerosol precursors in the field measurements, it is not surprising that there is some scatter in this plot that combines both lab and field data. Also, to match best with the field data, we note that only the data from Massoli *et al.* [2010] and Lambe *et al.* [2011a] that arise from the α -pinene precursor are included (as single points). Nevertheless, correspondence between the two quantities appears clear, extending down to low values of O:C. Thus, this study validates the postulate made earlier by Chang *et al.* [2010] that there is a connection between the two quantities. Indeed, the correspondence to the results from Whistler to those from Chang *et al.* [2010] may arise because biogenic SOA from monoterpene precursors was present at the CCN closure field site [Slowik *et al.*, 2010]. It is important to note, as mentioned by Jimenez *et al.* [2009], the $\kappa_{\text{org,CCN}}$ and overall composition from a variety of precursors may become increasingly similar with increasing O:C. Also, a similar molecular weight for many of the SOA precursors in Figure 3 will tend to lead to oxidation products of similar molecular weight, and thus similar hygroscopicities for the same O:C values.

4. Summary

[18] This study is the first direct measurement of the relationship between the degree of oxygenation and the CCN hygroscopicity of the organic component of ambient biogenic aerosol ($\kappa_{\text{org,CCN}}$) subject to OH oxidation, using novel methods for exposure to both gas- and aqueous-phase OH.

When combined with lab measurements, the results support a general linear relationship between the $\kappa_{\text{org,CCN}}$ of biogenic organic aerosols and their degree of oxygenation, as postulated by Chang *et al.* [2010], and shown previously to prevail for hygroscopic growth factors [Jimenez *et al.*, 2009]. The results emphasize that OH is an important aerosol oxidant. Additional field data with onsite OH processing should provide an indication of whether OH oxidation is the main organic aerosol aging process that drives the increases in hygroscopicity. While empirical in nature, this relationship provides a simple method for relating organic aerosol hygroscopicity to its composition, one that could potentially be included in atmospheric models. This trend needs to be further explored with ambient aerosol arising from a variety of sources, especially in urban and biomass burning regions, given that not all lab SOA precursors follow this relationship as closely [Massoli *et al.*, 2010; Lambe *et al.*, 2011a].

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