Relationship between aerosol oxidation level and hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles

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Relationship between aerosol oxidation level and hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles

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[1] Laboratory experiments investigated the relationship between oxidation level and hygroscopic properties of secondary organic aerosol (SOA) particles generated via OH radical oxidation in an aerosol flow reactor. The hygroscopic growth factor at 90% RH ($HGF_{90\%}$), the CCN activity ($\kappa_{ORG,CCN}$) and the level of oxidation (atomic O:C ratio) of the SOA particles were measured. Both $HGF_{90\%}$ and $\kappa_{ORG,CCN}$ increased with O:C; the $HGF_{90\%}$ varied linearly with O:C, while $\kappa_{ORG,CCN}$ mostly followed a nonlinear trend. An average $HGF_{90\%}$ of 1.25 and $\kappa_{ORG,CCN}$ of 0.19 were measured for O:C of 0.65, in agreement with results reported for ambient data. The κ_{ORG} values estimated from the $HGF_{90\%}$ ($\kappa_{ORG,HGF}$) were 20 to 50% lower than paired $\kappa_{ORG,CCN}$ values for all SOA particles except 1,3,5-trimethylbenzene (TMB), the least hygroscopic of the SOA systems. Within the limitations of instrumental capabilities, we show that differences in hygroscopic behavior among the investigated SOA systems may correspond to differences in elemental composition.

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1. Introduction

[2] The magnitudes of the direct and indirect effects exerted by aerosol particles on the Earth's radiation budget are influenced by their ability to take up water (changing the amount of scattered light) and to modify cloud properties by acting as cloud condensation nuclei (CCN). Including aerosol hygroscopicity in models is critical for improving aerosol forcing estimates [*Bates et al.*, 2006; *Massoli et al.*, 2009].

[3] A significant fraction of the global aerosol mass is represented by organic aerosol (OA) particles [*Zhang et al.*, 2007]. Typically, the average hygroscopic growth factor HGF (ratio of the diameter of a droplet in equilibrium with water vapor and its dry size in the sub-saturated regime) for secondary organic aerosol (SOA) particles is 1.2 ± 0.09 at relative humidity (RH) $\approx$ 90% and it is inversely proportional to the molecular weight of the gas-phase precursor [*Varutbangkul et al.*, 2006; *Gysel et al.*, 2007]. *Jimenez et al.* [2009] reported progressively larger HGF with increasing oxygen-to-carbon ratio O:C, a proxy for the aerosol oxidation level, for both ambient and laboratory SOA particles.

[4] The CCN potential of aerosol particles can be expressed via the parameter κ [*Petters and Kreidenweis*, 2007]. Depending on aerosol mixing state and oxidation level, the ambient organic fraction has hygroscopicity $0 < \kappa_{ORG} < 0.2$ [*Ervens et al.*, 2010, and references therein], with particles becoming more CCN active away from fresh pollution sources. *Shantz et al.* [2010] demonstrated that predictions of CCN growth kinetics for biogenic SOA improve upon assuming $\kappa_{ORG} = 0.20$.

[5] For organic aerosols, discrepancies between κ directly obtained by CCN activity measurements (hereafter $\kappa_{ORG,CCN}$) and κ estimated from HGF values ($\kappa_{ORG,\ HGF}$) have been observed [*Prenni et al.*, 2007; *Engelhart et al.*, 2008; *Roberts et al.*, 2010; *Irwin et al.*, 2010]. Recent studies suggested that measurements of HGF at RH > 95% are needed to determine the steepness of the HGF curve close to the point of CCN activation [*Wex et al.*, 2009; *Juranyi et al.*, 2009], and that factors such as gas-phase precursor concentration, molecular size, solubility and functional groups should be considered in predicting the CCN activity of SOA particles [*Duplissy et al.*, 2008; *Petters and Kreidenweis*, 2008; *Petters et al.*, 2009a, 2009b; *Poulain et al.*, 2010; *Good et al.*, 2010].

[6] Here we report a study that systematically correlates the HGF, $\kappa_{ORG,CCN}$, $\kappa_{ORG,HGF}$ and O:C of laboratory generated SOA particles.

2. Experimental Methods and Measurements

[7] Experiments were conducted using the Boston College aerosol flow reactor, a cylindrical chamber similar to the design of *Kang et al.* [2007]. SOA particles were generated via OH oxidation and homogeneous nucleation of gas-phase precursor species: α-pinene (proxy for biogenic SOA), 1,3,5-trimethylbenzene (TMB) and m-xylene (proxies for anthropogenic SOA) and a 50:50 mixture of α-pinene and m-xylene. OH radicals were produced by the reaction of excited oxygen [$O(^1D)$] atoms with water vapor at RH of 20 ± 2%. $O(^1D)$ atoms were produced from *in situ* UV photolysis of O_3 at $\lambda = 254$ nm using four mercury lamps. The integrated OH exposure was varied by stepping the

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lamp voltages from 0–110V, and it was estimated by monitoring the SO_2 decay in offline calibrations. Particles were generated at OH exposures of 2×10^{10}, 4.3×10^{11}, 8.4×10^{11} and 1.2×10^{12} molec cm^{-3} s (corresponding to 0.4, 5, 10 and 13 days of oxidative ageing at an ambient OH concentration of 1.5×10^{6} molec cm^{-3} [*Mao et al.*, 2009]), up to ten times higher than typical smog chamber studies [*Chhabra et al.*, 2010].

[8] The Aerodyne Research Inc. High-Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS) [*DeCarlo et al.*, 2006] was used to obtain atomic O:C and H:C ratios of the bulk submicron condensed-phase chemistry via elemental analysis [*Aiken et al.*, 2008]. The generated SOA particles had O:C ratios varying from 0.3 to 1.0, reaching values representative of highly oxygenated ambient particles. Table S1 of the auxiliary material gives the HR-ToF-AMS SOA mass loadings for each experimental condition.[1] The measurement accuracies for O:C and H:C, determined by comparison to laboratory standards, are 31% and 10%, respectively [*Aiken et al.*, 2008]. These values are an upper bound to the uncertainty of measurements of complex OA [*Chhabra et al.*, 2010]. The precision of the O:C and H:C measurements was ±15%.

[9] A hygroscopicity tandem differential mobility analyzer (HTDMA) instrument [*Liu et al.*, 1978] measured the hygroscopic growth factor HGF at 90% RH (hereafter $HGF_{90\%}$) as the ratio of wet (RH = 90%)-to-dry (RH < 10%) particle mobility diameters. $HGF_{90\%}$ values are reported for the dry diameter D_d = 50 nm. The stable operation of the HTDMA was routinely verified with ammonium sulfate. The absolute error (accuracy) in the $HGF_{90\%}$ values was 5%, the precision was 2%.

[10] The CCN activity of the SOA particles was measured with a Droplet Measurement Technologies CCN Counter [*Roberts and Nenes*, 2005] and it was expressed using the κ_{CCN} formulation of *Petters and Kreidenweis* [2007],

$$\kappa_{CCN} = \frac{4A^3}{27D_d^3 \ln^2 S_c}; \qquad A = \frac{4\sigma_w M_w}{RT\rho_w} \tag{1}$$

where S_c is the critical supersaturation, and M_w, ρ_w and σ_w are the molecular weight, density, and surface tension of water (σ_w = 0.072 J m^{-2}). Accuracy and precision in the CCN data were 15%. Additional information on particle generation, instrumentation and experimental methods are provided in the auxiliary material.

3. Results and Discussion

[11] The $HGF_{90\%}$ values of the SOA particles are reported in Figure 1 as a function of O:C. Data points are colored according to the integrated OH exposure. $HGF_{90\%}$ values increase with O:C for all of the SOA systems investigated, and vary from almost non-hygroscopic (1.05) to moderately hygroscopic (1.35). The $HGF_{90\%}$-to-O:C relationship is linear, although some $HGF_{90\%}$ values deviate slightly from the orthogonal regression (solid line) at O:C > 0.75. The m-xylene SOA particles exhibit the highest O:C (and $HGF_{90\%}$), consistent with smog chamber SOA data [*Chhabra et al.*, 2010]. α-pinene SOA generated from lower gas-phase precursor loading (40 ppb) have slightly higher O:C (and $HGF_{90\%}$) compared to α-pinene SOA generated at higher precursor loading (80 ppb), consistent with *Shilling et al.* [2009] and *Duplissy et al.* [2008].

[12] Our results agree with ambient HGF obtained at the Hyytiälä forest site [*Raatikainen et al.*, 2010] for low-volatility and semivolatile oxygenated organic aerosol particles (LVOOA and SVOOA, respectively [*Ng et al.*, 2010]) having the same dry diameter D_d = 50 nm. At O:C = 0.75, the HGF of the Hyytiälä LVOOA adjusted to 90% RH is 1.33 and it compares well with $HGF_{90\%}$ of 1.31 that we obtain at the same O:C.

[13] Figure 2 plots the $\kappa_{ORG,CCN}$ values as a function of O:C and shows that $\kappa_{ORG,CCN}$ increases with the O:C ratio. The m-xylene SOA is the most CCN active relative to other systems; the TMB SOA has the lowest $\kappa_{ORG,CCN}$, especially at O:C < 0.75. The $\kappa_{ORG,CCN}$ value of 0.22 ± 0.04 reported for ambient OOA at O:C of 0.59 [*Chang et al.*, 2010] agrees with our laboratory data within measurement uncertainties. For most data, the $\kappa_{ORG,CCN}$ does not vary linearly with O:C, as shown by the power fits to individual SOA systems (dotted lines). The $\kappa_{ORG,CCN}$-O:C relationship is steep at O:C > 0.75, whereas $\kappa_{ORG,CCN}$ is rather insensitive to O:C at O:C < ~0.5. Only for low-loading α-pinene SOA is the $\kappa_{ORG,CCN}$-O:C relationship almost linear. For reference, we show the κ_{CCN}-O:C parameterization of *Chang et al.* [2010] ($\kappa_{ORG,CCN}$ = (0.29 ± 0.05)*O:C) obtained for an O:C range of 0.3–0.6 (with $\kappa_{ORG,CCN}$ = 0 at O:C = 0). Such linear parameterization captures the data trend only partially because the $\kappa_{ORG,CCN}$ to O:C relationship is both non-uniform and SOA system-dependent, making it difficult to univocally predict the $\kappa_{ORG,CCN}$ from O:C.

[14] Figure 3 compares paired $\kappa_{ORG,CCN}$ and $\kappa_{ORG,HGF}$ values derived from $HGF_{90\%}$ using the κ-Köhler method [*Petters and Kreidenweis*, 2007]. Most $\kappa_{ORG,HGF}$ values are 20% to 50% lower than the corresponding $\kappa_{ORG,CCN}$ values, consistent with the result of *Prenni et al.* [2007] also shown in Figure 3. Recent theoretical modeling suggests that such deviations may reflect nonlinear changes in hygroscopic behavior at RH > 90% as a function of solute concentration [*Petters et al.*, 2009b; *Good et al.*, 2010]. However, the $\kappa_{ORG,CCN}$ and $\kappa_{ORG,HGF}$ for TMB SOA are in excellent agreement. Because the TMB particles have similar $HGF_{90\%}$ but lower $\kappa_{ORG,CCN}$ than the other SOA, one possible explanation is that TMB SOA particles undergo linear changes in hygroscopicity between sub and supersaturated regimes. *Duplissy et al.* [2008] reported good agreement between $\kappa_{ORG,CCN}$ and $\kappa_{ORG,HGF}$ values for both α-pinene and TMB SOA generated at near atmospheric loadings. Conversely, our results do not appear to be loading-dependent, as a similar level of agreement between $\kappa_{ORG,CCN}$ and $\kappa_{ORG,HGF}$ is seen, for instance, at all α-pinene concentrations ranging from 8 to 80 $\mu g/m^3$ (see Table S1 of the auxiliary material).

[15] Figure 4 plots the aerosol hydrogen-to-carbon ratio (H:C) versus O:C for the data shown in Figures 1–3. Our data display in the H:C versus O:C space in a similar way to that observed for multiple laboratory and field datasets [*Heald et al.*, 2010] We note that the TMB SOA particles have slightly higher H:C than the α-pinene, m-xylene and mixture SOA for the same O:C. This difference is most pronounced at low OH exposures (or O:C < 0.75), where the deviation in CCN activity between TMB and the other SOA

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[1] Auxiliary materials are available in the HTML. doi:10.1029/2010GL045258.

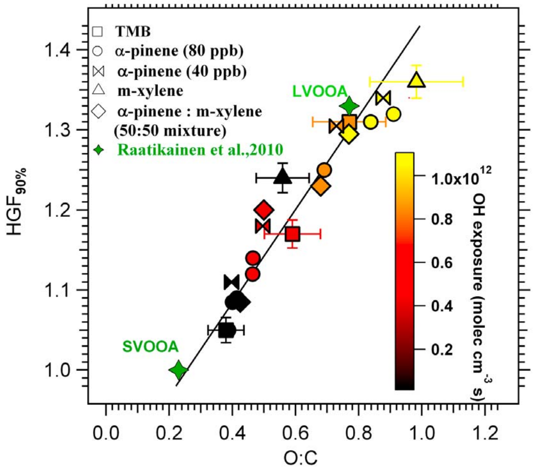

Figure 1. $HGF_{90\%}$ (D_d = 50 nm) vs. O:C for the laboratory SOA particles generated in this study. Markers are colored by integrated OH exposure. The solid line is the orthogonal regression through the dataset yielding $HGF_{90\%}$ = (0.58 ± 0.15)*O:C + (0.85 ± 0.08). The error bars (shown for m-xylene and TMB SOA only) represent a measurement precision of ±2% in $HGF_{90\%}$ and ±15% in O:C. HGF values for ambient SVOOA and LVOOA [*Raatikainen et al.*, 2010] scaled to 90%RH are also reported.

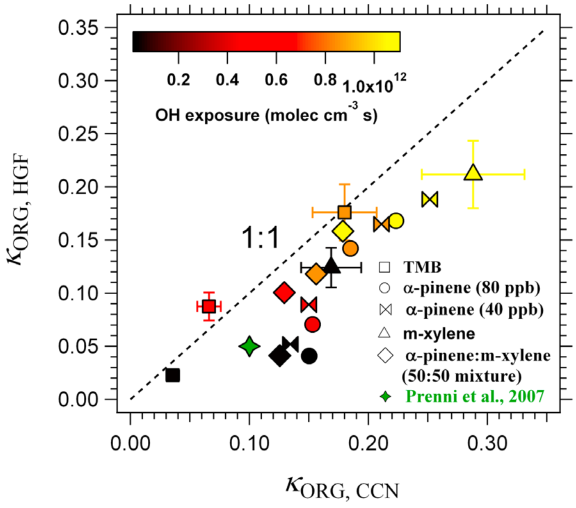

Figure 3. $\kappa_{ORG,HGF}$ vs $\kappa_{ORG,CCN}$ values for the laboratory SOA particles generated in this study. The error bars (shown for m-xylene and the TMB SOA only) represent measurement precision of ±15% in $\kappa_{ORG,CCN}$ and ±15% in $\kappa_{ORG,HGF}$. Literature data from *Prenni et al.* [2007] is shown for comparison.

systems is largest (Figure 2) and full mass spectra (not shown here) also exhibit significant differences. Recent work attributed the lower hygroscopicity of TMB SOA photo-oxidation products compared to that of α-pinene SOA to differences in molecular weight and functional groups [*Duplissy et al.*, 2010, and references therein]. Further molecular information will be needed to complement this result.

4. Summary and Conclusions

[16] We investigated the relationship between the oxidation level and the hygroscopic properties of laboratory SOA particles generated via OH radical oxidation in a flow reactor. The hygroscopic growth factor ($HGF_{90\%}$) and the CCN activity ($\kappa_{ORG,CCN}$) were measured over an O:C

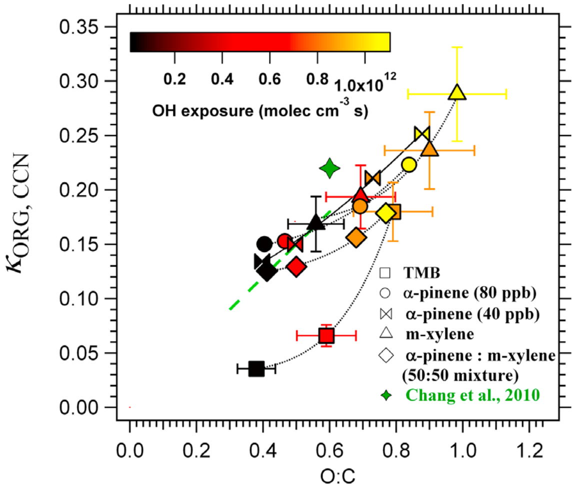

Figure 2. $\kappa_{ORG,CCN}$ vs O:C for the laboratory SOA particles generated in this study. The $\kappa_{ORG,CCN}$ for ambient OOA and the parameterization $\kappa_{ORG,CCN}$ = (0.29 ± 0.05) *O:C of *Chang et al.* [2010] (dashed line) are also plotted. Error bars (shown for m-xylene and TMB SOA only) represent measurement precision of ±15% in $\kappa_{ORG,CCN}$ and ±15% in O:C.

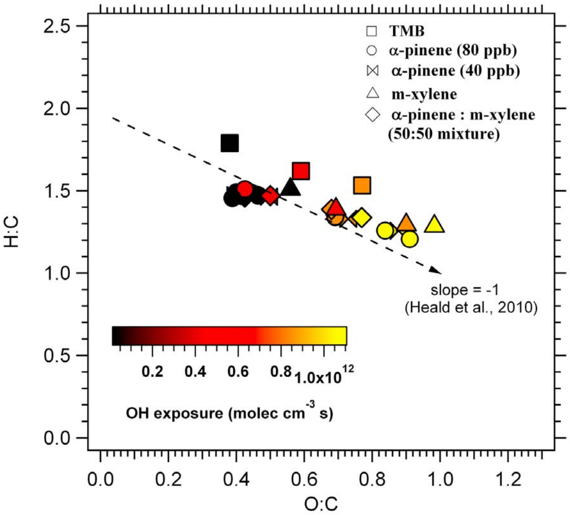

Figure 4. Elemental H:C vs O:C for the SOA systems plotted in Figures 1–3. For comparable OH exposure, the TMB particles have higher H:C than the other SOA types. The dashed line (H:C = 2, O:C = 1, from *Heald et al.* [2010]) is shown as a guide to the eye.

range of 0.3 to 1.0. We confirm the link existing between hygroscopic properties and chemical composition of SOA particles. $HGF_{90\%}$ values increased linearly with O:C for all SOA systems. $\kappa_{ORG,CCN}$ also increased as a function of O:C, but this relationship appeared to be system-dependent and not a linear one. At comparable O:C, our $HGF_{90\%}$ and $\kappa_{ORG,CCN}$ values are in good agreement with ambient data for organic-dominated aerosol particles. The $\kappa_{ORG,HGF}$ values were 20 to 50% lower than $\kappa_{ORG,CCN}$ except for the TMB SOA, which also produced the less CCN active SOA particles. We observed difference in the elemental composition between TMB and the other SOA systems that may relate to different hygroscopic behaviors. Based on these laboratory results, we provide a semi-empirical parameterization of $HGF_{90\%}$ vs. O:C, whereas a univocal parameterization for the $\kappa_{ORG,CCN}$ vs. O:C relationship was difficult to establish. Such trends observed for laboratory generated SOA systems should be tested with ambient data to determine if and to what extent a relationship between aerosol hygroscopicity and oxidation level can be defined in a simple manner and perhaps generalized for use in model parameterizations.

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