Oxidative aging and cloud condensation nuclei activation of laboratory combustion soot

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Abstract

Radiative forcing by aerosol particles containing black carbon (BC) may be positive or negative depending on specific atmospheric conditions. Black carbon itself absorbs solar radiation and thereby heats the surrounding environment. On the other hand, as a result of atmospheric aging, BC-containing particles may become hydrophilic due to oxidation, condensation, and/or coagulation of water-soluble material. The aged particles can act as cloud condensation nuclei (CCN) and contribute to cloud formation that may result either in cooling or heating. In this work, through a series of laboratory experiments, we investigate the transformation of soot particles from hydrophobic to hydrophilic and estimate the atmospheric residence time required for this transformation. Ethylene flame-generated soot particles were size-selected and exposed to OH radicals in a Potential Aerosol Mass flow

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reactor. Aging was simulated via OH exposures equivalent to atmospheric lifetimes over a range from hours to multiple days. The chemical composition of the organic coatings as a function of OH exposure was monitored with an Aerodyne Aerosol Mass Spectrometer. The CCN activity of the aged soot particles was measured as a function of OH exposure and chemical composition. Experimental measurements indicate that heterogeneous OH oxidation of initially CCN-inactive nascent soot produces CCN-active particles. Critical supersaturations at integrated OH exposures equivalent to 0.4, 2, and 10 days are 2.1%, 0.82%, and 0.40%. Corresponding values for the effective hygroscopicity parameter, κ_{eff} , ranged from $\kappa_{\text{eff}} < 8 \times 10^{-4}$ to $\kappa_{\text{eff}} = 0.09$ as a function of OH exposure. Condensation of hydrophilic organic or inorganic coatings (produced from oxidation of gas-phase precursors introduced to the flow reactor) on soot particles speeds up the CCN activation by a factor of 6 to 50 depending on the nature and thickness of the coating. The results suggest that CCN activation of atmospheric BC-containing particles is primarily due to secondary coatings.

Key words:

soot, oxidative aging, cloud condensation nuclei

1. Introduction

Aerosol particles affect climate through direct and indirect interactions (Mahowald, 2011). Direct interactions consist of scattering or absorption by the particles of solar radiation. Indirect interactions are due to the role of hydrophilic aerosols in cloud formation and cloud lifetime. Clouds may either cool or warm the atmosphere depending on atmospheric conditions.

7 While the climate impact of inorganic components of aerosol particles
8 (e.g. sulfates, nitrates, and mineral dust) is reasonably well understood,
9 aerosol particles containing organic and BC components are not adequately
10 characterized for reliable assessment of their climate effects. The interac-
11 tion of particles containing absorbing material such as black carbon (BC)
12 is especially complex. Black carbon absorbs solar radiation and thereby
13 heats the surrounding environment, leading to atmospheric warming and
14 surface dimming (Reddy and Boucher, 2007; Ramanathan and Carmichael,
15 2008; Andreae and Ramanathan, 2013). On the other hand, as a result of
16 atmospheric aging processes, hydrophobic BC-containing particles may be-
17 come hydrophilic due to oxidation of initially present hydrophobic coatings
18 (Chughtai et al., 1996, 1999; Zuberi, 2005), condensation of hydrophilic mate-
19 rial, (Hings et al., 2008; Khalizov et al., 2009; Tritscher et al., 2011; Qiu et al.,
20 2012; Khalizov et al., 2013), or through coagulation with hydrophilic particles
21 (Hagen et al., 1991; Podzimek et al., 1991; Fierce et al., 2013). In this way,
22 BC-containing particles become cloud condensation nuclei (CCN). In the ab-
23 sence of aging processes, fresh BC particles containing hydrophilic coatings
24 (e.g. produced from combustion of fuels with sufficient sulfur content; Gysel
25 (2003)) may also contribute to CCN formation. The CCN-activated soot
26 particles contribute to cloud formation resulting in cooling or warming de-
27 pending on atmospheric conditions and soot content. CCN activation may
28 also affect particle atmospheric lifetime via wet deposition.

29 The deliquescence of soot particles coated with hydrophilic organics ap-
30 proaches the hygroscopicity of the pure organics at large coating thickness
31 (Hings et al., 2008; Wittbom et al., 2014). However, these previous studies

32 have not directly connected changes in soot chemical composition and pho-
33 tochemical age to changes in CCN activity. Thus, the available data are not
34 readily implemented in climate models. To date, models typically simulate
35 aging of soot using highly simplified parameterizations because the depen-
36 dence of BC hygroscopicity on physicochemical properties is highly uncertain.
37 For example, Cooke et al. (1999) assumed conversion of hydrophobic BC to
38 hydrophilic BC takes 1.15 days, a timescale that has been widely used in
39 modeling BC aging processes (Chin et al., 2002). However, recent field stud-
40 ies suggest that this conversion can occur over significantly faster timescales
41 (Moffet and Prather, 2009; Schwarz et al., 2010; Cheng et al., 2012).

42 The present work is focused on quantitatively relating oxidative and con-
43 densational aging to CCN activity of soot particles. Laboratory generated
44 ethylene flame soot particles were exposed to OH radicals in a flow reactor.
45 Aging was simulated via OH exposures equivalent to atmospheric lifetimes
46 over a range from hours to multiple days. The chemical composition of the
47 organic coatings as a function of OH exposure was measured with an aerosol
48 mass spectrometer. The CCN activity of the aged soot particles was mea-
49 sured as a function of OH exposure and chemical composition. Experiments
50 were performed with both nascent soot and soot particles coated by sec-
51 ondary organic aerosol (SOA) representative of biogenic and anthropogenic
52 compounds found in the atmosphere and by sulfuric acid. The coatings were
53 produced from oxidation of gas-phase precursors added to the flow reac-
54 tor along with the soot. The measurements were used to estimate, under a
55 range of atmospherically relevant conditions, residence times required for BC
56 containing particles to become CCN-active and to formulate values for the

57 effective hygroscopicity parameter κ_{eff} .

58 2. Materials and Methods

59 Figure 1 is a schematic of the experimental setup showing soot generation,
60 oxidation, monitoring and characterization.

61 2.1. Soot Generation

62 Soot particles were generated using a premixed flat burner flame as de-
63 scribed in detail elsewhere (Slowik et al., 2007; Cross et al., 2010). Briefly,
64 premixed flows of ethylene, oxygen, and nitrogen gases are delivered through
65 a McKenna flat burner at a total flow of 9 L/min, with a fuel-to-air ratio,
66 $\phi = 2.00 \pm 0.05$. A mini-eductor (Fox Valves) extracts a flow of polydisperse
67 soot particles from the tip of the flame into the differential mobility analyzer
68 (DMA, TSI 3081) to select monodisperse soot particles. The flow passes into
69 a charcoal denuder to remove gas-phase organics.

70 2.2. Particle Processing

71 Soot particles were exposed to OH radicals in a Potential Aerosol Mass
72 (PAM) flow reactor (Kang et al., 2007; Lambe et al., 2011a). The average
73 residence time was approximately 100 sec, and the level of processing (i.e.
74 exposure time) was controlled by the OH concentration in the reactor. OH
75 radicals were produced via the reaction $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$, with $\text{O}(^1\text{D})$
76 radicals produced via the photodissociation $\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(^1\text{D})$. The UV
77 light was produced by four mercury lamps (BHK Inc.) inside the PAM reac-
78 tor with peak emission intensity at $\lambda = 254$ nm. These lamps were mounted
79 in teflon-coated quartz cylindrical sleeves and were continually purged with

80 N₂. O₃ was generated outside the PAM reactor by irradiating O₂ with a mer-
81 cury lamp ($\lambda = 185$ nm). Water vapor was introduced using a heated Nafion
82 membrane humidifier (Perma Pure LLC). The humidifier temperature was set
83 to provide a controlled relative humidity (RH) in the range of 24%-30%.

84 The OH concentration was determined by measuring the decay of SO₂
85 due to the well-characterized reaction with OH (Davis et al., 1979). The OH
86 exposure is the product of the OH concentration and the average residence
87 time in the PAM reactor. The OH concentration was varied by changing
88 the UV light intensity by step-wise changing the lamp voltages. The deple-
89 tion of OH within the PAM reactor due to reactions with aerosol particles
90 is negligible (less than $\sim 5\%$). The OH exposures ranged from 4.9×10^{10} to
91 1.3×10^{12} molec cm⁻³ s; approximately equivalent to 0.4 to 10 days of atmo-
92 spheric exposure at a OH concentration of 1.5×10^6 molec cm⁻³ typical of 24
93 hour-averaged continental OH levels (Mao et al., 2009). In the experiments
94 studying the effect of secondary organic aerosol and sulfuric acid coatings,
95 gas-phase α -pinene, *m*-xylene, or SO₂ was introduced along with the soot to
96 produce SOA or sulfuric acid via OH oxidation inside the PAM reactor. The
97 α -pinene and *m*-xylene precursors were chosen as surrogate species for bio-
98 genic and anthropogenic emissions, respectively. The oxidized vapors formed
99 a deposition coating on the soot particles.

100 2.3. Particle Monitoring and Characterization

101 Particle mobility size distributions were measured with a scanning mobil-
102 ity particle sizer (SMPS, TSI 3080). Mass spectra and aerodynamic size dis-
103 tributions of the non-refractory component were measured with an Aerodyne
104 compact time-of-flight aerosol mass spectrometer (c-ToF-AMS) (Drewnick

et al., 2005). The CCN activation of soot particles was measured using a continuous flow CCN counter (CCNC, Droplet Measurement Technologies) (Roberts and Nenes, 2005; Lance et al., 2006). Prior to CCN measurements, the aerosol was size-selected by a DMA, after which CCN activation curves were generated by systematically varying the CCNC column temperature gradient to obtain controlled water vapor supersaturation between 0.1-1.8%.

3. Results and Discussion

3.1. Mass spectra of nascent and oxidized flame soot

Figure 2 shows typical AMS spectra of organics associated with nascent and oxidized flame soot, respectively. To present the spectra on the same scale, signals at $m/z > 90$ are scaled by a factor of 40. All signals are normalized to the particle mass (M_p) which was calculated using the mass concentration measured by the c-ToF-AMS and the integrated number concentration measured by the SMPS. Combined AMS and SMPS measurements suggest that under the flame conditions used in the current experiments the non-refractory component comprises 5%-10% of M_p , with the remaining mass consisting of BC that is not directly detected with the c-ToF-AMS. The spectrum shown in Figure 2c was generated at the maximum OH exposure used in these experiments (1.3×10^{12} molec cm^{-3} s). The mass spectra shown in Fig. 2 have a regularly spaced pattern of aromatic fragments from $m/z = 198$ to 374 (purple sticks in figure) characteristic of unoxidized polycyclic aromatic hydrocarbons (NIST Chemistry Webbook) and their accompanying doubly-charged ions which contribute to signals measured $m/z = 99$ to 187. Additional contributions from aliphatic ions were also present and are

commonly observed in flame soot (Cain et al., 2010). Figures 2b and 2c show that the oxidized organics are dominated by $m/z = 44$ (CO_2^+), which is a mass spectral fragment of organic carboxylic acids measured in the AMS (Aiken et al., 2008).

A comparison of Figures 2a, 2b and 2c shows a clearly evident feature of the mass spectra: the oxidative loss of polycyclic aromatic hydrocarbons (PAHs). Mass spectra such as shown in Figure 2 were obtained for three OH exposures: 4.9×10^{10} , 2.5×10^{11} and 1.3×10^{12} molec cm^{-3} s. The effect of O_3 on the mass spectrum of the soot was similar to the effect of OH but significantly smaller. For the spectra shown in Figure 2, the mass-per-particle of PAHs ($M_{p,PAH}$) decreases as a function of OH exposure from 0.011 fg for nascent soot to 0.0041 fg for oxidized soot. This corresponds to a decrease in the total mass fraction of PAHs from 0.0059 to 0.0020, and a decrease in the non-refractory mass fraction of PAHs from 0.31 to 0.026. On the other hand, the mass per particle of non-refractory organics exclusive of PAH compounds ($M_{p,nPAH}$) increases from 0.023 fg for nascent soot to 0.15 fg for oxidized soot, or an increase in the total mass fraction of non-PAH organics from 0.013 to 0.076, and an increase in the non-refractory mass fraction from 0.69 to 0.97. This increase in $M_{p,nPAH}$ as a function of OH exposure is larger than the decrease in $M_{p,PAH}$. Because no volatile organic compounds (VOCs) were added with the BC in these experiments to produce SOA, this net increase in non-refractory M_p may be explained by functionalization of surface-bound PAH/aliphatic compounds to organic acids.

152 3.2. CCN activity of oxidized soot

153 Figure 3 shows the CCN activation ratio of plotted as a function of water
 154 vapor supersaturation in the range from 0.1% to 1.8%. The mobility diam-
 155 eter of the soot particles prior to activation was 222 nm, corresponding to a
 156 volume equivalent diameter (D_{ve}) of approximately 124 nm (see Section 3.3).
 157 CCN activation curves for flame soot particles were obtained for three OH
 158 exposures; 4.9×10^{10} , 2.5×10^{11} and 1.3×10^{12} molec cm⁻³ s as shown. The
 159 figure also shows the calculated CCN activation of ammonium sulfate parti-
 160 cles with $D_{ve} = 124$ nm (Petters and Kreidenweis, 2007) and CCN activation
 161 measurements for nascent (unoxidized) soot and soot exposed to ~ 20 ppm
 162 O₃, or an integrated O₃ exposure of about 5×10^{16} molec cm⁻³ s, which is the
 163 level of O₃ used to generate OH. This integrated O₃ exposure was obtained in
 164 the dark with the lamps turned off and corresponds to 1.25 days of equivalent
 165 ambient O₃ oxidation at a typical average O₃ concentration of 5×10^{11} molec
 166 cm⁻³ (20 ppb) (Hough and Derwent, 1990). As expected, nascent soot is
 167 CCN-inactive in the range of supersaturations studied (up to 1.8%). Below
 168 a supersaturation of about 1%, CCN activation of soot particles exposed to
 169 ozone at the ozone concentration used in our studies is small. Subsequent
 170 data are corrected for partial activation of soot by O₃ oxidation. CCN ac-
 171 tivation curves such as shown in Figure 3 are usually characterized by the
 172 critical supersaturation, s_c , at which the Kelvin effect exceeds the solute ef-
 173 fect leading to spontaneous growth of a particle to become a cloud droplet.
 174 As is usual, s_c is designated by water vapor supersaturation at which the
 175 activation ratio equals 0.5.

176 Figure 4a shows s_c obtained from data in Figure 3 for oxidized soot as

177 a function of OH exposure (lower axis). The upper axis shows the equiv-
 178 alent photochemical age in days assuming an average OH concentration of
 179 1.5×10^6 molec cm⁻³. In this figure, the contribution of the O₃ oxidation to
 180 CCN activation was taken into account by subtracting the activation ratio
 181 of soot particles exposed to O₃ below $s_c = 1\%$ from all other CCN activation
 182 curves. This correction was significant only for the lowest OH exposure stud-
 183 ied and was necessary because O₃ uptake by PAHs on the soot was significant
 184 compared to OH uptake at this condition (Bertram et al., 2001; Gross and
 185 Bertram, 2008; Shiraiwa et al., 2009; Bedjanian et al., 2010). The solid line
 186 in the figure is a power law fit to the three points shown. Figure 4a shows
 187 that s_c of oxidized soot within 0.1% of the minimum s_c that was measured
 188 (corresponding to maximum CCN activation) after approximately 6 days of
 189 equivalent atmospheric exposure at the assumed OH concentrations.

190 3.3. Effective hygroscopicity parameter (κ_{eff}) values of oxidized soot

191 The dependence of CCN activation of a particle on chemical composition
 192 (in our case level of oxidation via OH exposure) can be expressed in terms of
 193 a parameter κ that is often used in global models to represent hygroscopicity.
 194 This parameter is obtained via the κ -Köhler equation (Petters and Kreiden-
 195 weis, 2007; Sullivan et al., 2009) and is defined for a spherical particle by
 196 Equation 1:

$$\kappa = \frac{4A^3}{27D_d^3 \ln^2 s_c}; A = \frac{4\sigma_w M_w}{RT\rho_w} \quad (1)$$

197 Here s_c is the previously defined critical supersaturation, expressed as a frac-
 198 tion rather than a percentage; D_d is the droplet diameter of the dry particle,

199 M_w is the molecular weight of water, R is the universal gas constant, T is
 200 the temperature, and ρ_w is the density of water; A is a constant equal to
 201 2.1×10^9 m assuming the liquid water surface tension of 0.072 J m^{-2} at $T =$
 202 298 K. We note that κ -Köhler theory implicitly accounts for multiple soluble
 203 and insoluble components in a mixed particle. Here, because black carbon
 204 is insoluble, we note that our calculated κ -values are instead overall effective
 205 κ -values (κ_{eff}) that are the linear combination of the different components'
 206 volume-fraction-weighted κ -values.

207 The κ -values as formulated in Equation 1 are a function of the diameter
 208 of a spherical particle. However, the value of the diameter to be used for
 209 fractal soot particles is not evident. SMPS and AMS measurements yield
 210 the mobility and vacuum aerodynamic diameter values, D_m and D_{va} that
 211 are functional expressions rather than geometric parameters. Using D_m and
 212 D_{va} , the volume equivalent diameter D_{ve} can be calculated defined as the
 213 volume of a sphere with the same volume as the particle. In the absence
 214 of more detailed information, we will, as is usual (Tritscher et al., 2011; Liu
 215 et al., 2013; Wittbom et al., 2014), use the volume equivalent diameter (D_{ve})
 216 in calculating κ_{eff} . In our experiments $D_{ve} \approx 124 \pm 6$ nm and did not change
 217 substantially in the course of oxidation. Equations used to calculate D_{ve} are
 218 presented in Appendix A. Each of the s_c values measured as a function of
 219 OH exposure can yield a value of κ_{eff} via Equation 1.

220 In Figure 4b, we show κ_{eff} as a function of OH exposure and photochem-
 221 ical age calculated using Equation 1 with s_c as shown in Figure 4a and D_{ve}
 222 $= 124$ nm. The calculated κ_{eff} -value increases from $\kappa_{\text{eff}} < 8 \times 10^{-4}$ at low
 223 OH exposure to $\kappa_{\text{eff}} = 0.09$ at the highest OH exposure, compared to $\kappa_{\text{eff}} \approx$

0.1 – 0.2 for hydrophilic organic compounds and secondary organic aerosol (SOA) (Petters et al., 2009; Lambe et al., 2011b; Mei et al., 2013; Rickards et al., 2013). Equation 1 illustrates the size dependence of CCN activation of oxidized soot particles. Figure 4c shows calculated s_c values obtained from κ_{eff} -values in Figure 4b for two volume equivalent diameters, $D_{ve} = 100$ nm and $D_{ve} = 200$ nm, used here as reference values for urban and remote BC, respectively (Schwarz et al., 2006; Liu et al., 2010; Ohata et al., 2013; Schwarz et al., 2013). At one day of equivalent atmospheric oxidation, calculated s_c values range from 0.6% ($D_{ve} = 200$ nm) to 1.7% ($D_{ve} = 100$ nm). Similar size dependence is predicted at other OH exposures with the simplifying assumption that the heterogeneously oxidized surface-to-BC volume ratio remains constant as a function of particle size. Typical maximum supersaturations in atmospheric cumulus clouds range from 0.3% to 0.8% (Pruppacher and Klett, 1980).

3.4. Effect of SOA and sulfuric acid coatings on CCN activation of soot

In a subset of experiments, SO_2 , α -pinene or m -xylene was introduced along with soot into the PAM reactor. These species were oxidized in the gas phase to produce sulfuric acid or SOA, which condensed to coat the soot. The coating thickness ranged from approximately 2 to 66 nm. While the same mobility diameter was always size-selected prior to CCN measurements independent of coating thickness ($D_m \sim 222$ nm), coating the soot with sulfuric acid or SOA increases D_{va} , and, consequently, D_{ve} , though only changing the soot core mass slightly.

Figure 5 shows s_c as a function of OH exposure for soot particles coated with sulfuric acid or SOA produced by oxidation of gas phase α -pinene and

249 *m*-xylene. The coating thickness is designated by color as shown in the figure.
 250 The solid line is the critical supersaturation for uncoated soot duplicated from
 251 Figure 4a. The effects of sulfuric acid and SOA coatings on s_c were measured
 252 at three OH exposures and varied coating thickness. Figure 5 shows that s_c
 253 for coated soot is lower than for uncoated soot at a specific OH exposure, as
 254 expected (Hings et al., 2008; Tritscher et al., 2011; Qiu et al., 2012; Khalizov
 255 et al., 2013; Ma et al., 2013). Ozone is highly efficient at oxidizing α -pinene.
 256 This is made evident by the fact that CCN activation of soot coated with
 257 SOA formed from α -pinene ozonolysis alone occurs at $s_c = 0.37\%$ and does
 258 not increase substantially with OH exposure. Not surprisingly, sulfuric acid
 259 coatings are highly effective at reducing the critical supersaturation of soot
 260 particles; the theoretical $s_c = 0.11\%$ for pure ammonium sulfate particles
 261 with $D_{ve} = 124$ nm is shown for reference assuming $\kappa = 0.6$ (Petters and
 262 Kreidenweis, 2007). Figure 5 suggests that soot particles studied in this
 263 work are maximally activated by an SOA coating thickness of 50 nm or less,
 264 or a sulfuric acid coating thickness of 10 nm or less.

265 4. Atmospheric Implications

266 Average reported nanoparticle growth rates range from approximately 2
 267 to 5 nm/hr (clean rural) and 7 to 18 nm/hr (polluted urban) (Yli-Juuti et al.,
 268 2011; Pierce et al., 2012; Westervelt et al., 2013). Corresponding atmospheric
 269 timescales to achieve these organic coating thicknesses leading to maximal
 270 CCN activation are about 10 – 25 hr in clean air and 3 – 7 hr in polluted air, or
 271 a factor of 6 – 50 times faster than a similar level of CCN activity reached by
 272 soot particles that were oxidized by OH (~ 6 days). Regardless of whether the

273 decrease in s_c following SOA condensation occurs because of changes in the
274 volume fraction or hygroscopicity (i.e., κ) of either the soot or soluble coating
275 (or both), the relative timescales of these aging processes suggest that under
276 typical conditions, increases in hygroscopicity of BC-containing particles in
277 the atmosphere leading to CCN activation are dominated by condensation of
278 secondary coatings rather than heterogenous oxidation. Our laboratory mea-
279 surements support recent field studies suggesting that CCN activation of BC
280 particles is dependent upon SOA formation/deposition rates, and may occur
281 on timescale of hours (Moffet and Prather, 2009; Schwarz et al., 2010; Cheng
282 et al., 2012), implying that the climate impacts of BC-containing particles
283 may be substantially different than predicted by current models. Our results
284 can be used as inputs to models to refine CCN and lifetime predictions of
285 freshly coated BC-containing particles as a function of atmospheric age and
286 SOA coating thickness.

287

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298 A. Soot particle volume equivalent diameter calculations

299 Some information about effects of oxidation, denuding, and coating of
 300 the soot particles is provided by the dynamic shape factor, χ (Slowik et al.,
 301 2007):

$$\chi = \frac{\text{Drag on particle}}{\text{Drag on sphere of equal volume}} \quad (2)$$

302 By definition, $\chi = 1$ for a spherical particle.

303 In the free-molecular flow regime, χ is related to the particle vacuum
 304 aerodynamic diameter D_{va} and the volume equivalent diameter, D_{ve} , de-
 305 fined as the volume of a sphere with the same volume as the particle. The
 306 relationship is shown in Equation 3:

$$D_{va} = D_{ve} \frac{\rho_p}{\rho_0} \frac{1}{\chi_v} \quad (3)$$

307 where ρ_p is the particle density, ρ_0 is unit density (1 g cm^{-3}), and χ_v is the
 308 dynamic shape factor in the free-molecular flow regime.. We assumed $\rho_p =$
 309 1.8 g cm^{-3} for black carbon, $\rho_p = 1.3 \text{ g cm}^{-3}$ for PAHs, $\rho_p = 1.4 \text{ g cm}^{-3}$ for
 310 non-PAH organics, and $\rho_p = 1.77 \text{ g cm}^{-3}$ for sulfates. The particle mobility
 311 diameter, D_m , is measured by the SMPS and is related to D_{ve} as shown in
 312 Equation 4:

$$D_m = D_{ve} \frac{C_c(D_m)}{C_c(D_{ve})} \chi_t \quad (4)$$

313 The $C_c(D)$ parameters are the Cunningham slip correction factors, which
 314 account for the reduced drag on a particle in the transition and free-molecular
 315 flow regimes; χ_t is the dynamic shape factor in the transition regime. The

316 measured quantities – D_{va} and D_m , and the mass of the non-refractory com-
 317 ponents of the soot particles – are used in a system of equations to determine
 318 particle mass, particle density, volume, and dynamic shape factor (assuming
 319 $\chi = \chi_v = \chi_t$) as shown in Equations 5 – 7:

$$d_{va} = \frac{d_{ve}}{\chi \rho_0} \left(\frac{M_{BC} + M_{PAH} + M_{AL}}{\frac{M_{BC}}{\rho_{BC}} + \frac{M_{PAH}}{\rho_{PAH}} + \frac{M_{AL}}{\rho_{AL}}} \right) \quad (5)$$

$$\frac{M_{BC}}{\rho_{BC}} + \frac{M_{PAH}}{\rho_{PAH}} + \frac{M_{AL}}{\rho_{AL}} = \frac{\pi}{6} \times d_{ve}^3 \quad (6)$$

$$M_p = C \times d_m^{D_f} \quad (7)$$

320 Here M_p is the mass per particle, ρ is the material density of the particle
 321 components, and D_f is the mass mobility exponent. The subscripts 'BC',
 322 'PAH', and 'AL' refer to black carbon, polycyclic aromatic hydrocarbon,
 323 and aliphatic hydrocarbon components, respectively. We derived χ -values
 324 ranging from 2.47 to 2.88 for nascent soot and 2.21 to 2.71 for oxidized soot
 325 in the absence of SOA formation, whereas SOA-coated soot had χ -values
 326 ranging from 1.07 to 2.42.

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Figure 1: Schematic showing production, processing, and characterization of ethylene flame soot particles. Ethylene combustion in O_2 by a McKenna flat burner produces soot that is sampled using a mini-eductor to extract polydisperse soot particles from the tip of the flame into a Differential Mobility Analyzer (DMA) where the particles are size-selected. The flow then passes through an annular charcoal denuder. Sample flow is then mixed with humidified N_2 , O_2/O_3 , and gas-phase SOA precursor and aged in a Potential Aerosol Mass (PAM) reactor prior to characterization with Scanning Mobility Particle Sizer (SMPS), compact time-of-flight aerosol mass spectrometer (c-ToF-AMS), and cloud condensation nucleus counter (CCNC).

Figure 2: AMS spectra of non-refractory components of (a) nascent soot and soot exposed to OH at exposures of (b) 2.5×10^{11} and (c) 1.3×10^{12} molec cm $^{-3}$ sec. Spectra are normalized to particle mass (M_p). Signals at $m/z > 90$ are scaled by a factor of 40 to present spectra on the same display.

Figure 3: CCN activation curves for nascent soot, soot oxidized by O_3 , and soot oxidized by OH. The mobility diameter of the soot particles prior to activation was 222 nm. Error bars indicate $\pm 1 \sigma$ of replicate measurements. The calculated CCN activation of ammonium sulfate with the same volume equivalent diameter ($D_{ve} = 124 \text{ nm}$) is shown for reference.

Figure 4: (a) Measured CCN critical supersaturation (s_c) values (solid line is best-fit curve to the data) and (b) calculated CCN κ_{eff} -values as a function of OH exposure for oxidized soot particles with $D_{ve} = 124$ nm. (c) Calculated s_c values as a function of OH exposure for oxidized soot particles with $D_{ve} = 100$ nm and 200 nm bracketing the measured D_{ve} (see Section 3.3). Equivalent photochemical age is shown on the top axis assuming an average atmospheric OH concentration of 1.5×10^6 molec cm⁻³. Error bars indicate $\pm 1 \sigma$ of replicate measurements.

Figure 5: Measured CCN critical supersaturation (s_c) values as a function of photochemical age for oxidized soot particles with initial volume equivalent diameter $D_{ve} = 124$ nm coated by sulfuric acid, α -pinene SOA, and m -xylene SOA. For ozonolysis conditions, photochemical age was calculated assuming an average atmospheric O_3 concentration of 5×10^{11} molec cm^{-3} .